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APPLICATION FOR U.S. LETTERS PATENT

Title:

LIQUID ADJUVANTS

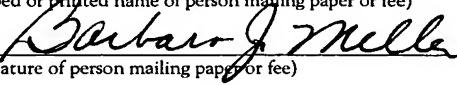
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## Description

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## Liquid adjuvants

The present invention relates to novel liquid adjuvants, in particular to those which are advantageously suitable for the field of crop protection, for example in  
10 combination with agrochemical active substances.

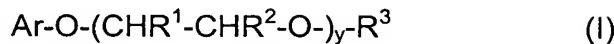
Agrochemical active substances, in particular agrochemical active substances which are applied post-emergence and taken up into the plants via the leaf, for example post-emergence herbicides, are frequently mixed with what are known as adjuvants,  
15 for example in order to increase the biological activity of the agrochemical active substances. Adjuvants, in this context, are understood as meaning substances which enhance the biological activity while not being bioactive themselves.

This technology is used widely in practice and is described intensively in the  
20 specialist literature (see, for example, C.L.Foy, D.W. Pritchard (Ed.), "Pesticide Formulation and Adjuvant Technology", CRC Press, Inc, 1996, Boca Raton, Florida, USA; C.L. Foy (Ed.), "Adjuvants for Agrochemicals, CRC Press, Inc, 1992, Boca Raton, Florida, USA). Thus, it is known, for example, to mix sulfonylureas with vegetable-oil-based adjuvants, which are also commercially available  
25 (WO 01/30155).

It was an object to provide novel adjuvants which have advantageous properties, in particular in combination with agrochemical active substances such as herbicides.  
30 Surprisingly, it has now been found that this object is achieved by the specific adjuvants of the present invention.

The present invention thus relates to a liquid adjuvant comprising

a) one or more surfactants of the formula (I)

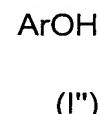
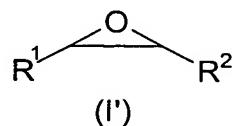


where

- 5 Ar is aryl which is substituted by at least two, preferably 2 to 10, ( $\text{C}_1\text{-C}_{30}$ )alkyl radicals,  
 R<sup>1</sup> is H or ( $\text{C}_1\text{-C}_6$ )alkyl,  
 R<sup>2</sup> is H or ( $\text{C}_1\text{-C}_6$ )alkyl,  
 R<sup>3</sup> is H, an unsubstituted or substituted ( $\text{C}_1\text{-C}_{30}$ ) hydrocarbon radical,  
 10 preferably ( $\text{C}_1\text{-C}_{30}$ )alkyl, ( $\text{C}_2\text{-C}_{30}$ )alkenyl or ( $\text{C}_2\text{-C}_{30}$ )alkynyl, a sulfonate radical, a phosphonate radical, an acyl radical, and  
 y is an integer from 1 to 100, preferably 1 to 20, and

b) one or more fatty acid esters.

- 15 If  $y > 1$  in the surfactants of the formula (I), the y units ( $\text{CHR}^1\text{-CHR}^2\text{-O}$ ) can be identical (for example ethylene oxide homopolymer units, propylene oxide homopolymer units or butylene oxide homopolymer units) or different from one another (for example ethylene oxide/propylene oxide copolymer units or ethylene oxide/butylene oxide copolymer units). Surfactants of the formula (I) are generally known and also commercially available, for example those from the Sapogenat® T series by Clariant AG. Moreover, surfactants of the formula (I) can be prepared by known reactions, for example surfactants of the formula (I) where  $\text{R}^3 = \text{H}$  by reaction of commercially available epoxides, for example those of the formula (I'), with  
 20 hydroxyl aromatics, for example those of the formula (I''), under catalytical conditions (for example NaOH and/or sodium acetate; temperature approx. 100 - 200°C; superatmospheric pressure of approx. 2 – 10 bar).



30

The radicals R<sup>1</sup> and R<sup>2</sup> in formula (I') and the radical Ar in formula (I'') are as defined in formula (I). Surfactants of the formula (I) where  $\text{R}^3 \neq \text{H}$  can be obtained from

- surfactants of the formula (I) where  $R^3 = H$  by standard reactions. For example, surfactants of the formula (I) where  $R^3 =$  (substituted) hydrocarbon radical such as alkyl, alkenyl or alkynyl can be obtained by alkylation, alkenylation or alkynylation, for example with alkyl halides, alkenyl halides or alkynyl halides, with base catalysis;
- 5 those where  $R^3 =$  sulfonate radical can be obtained by sulfatation followed by neutralization; those where  $R^3 =$  phosphonate radical can be obtained by phosphatation; those where  $R^3 =$  acyl radical can be obtained by acylation.

These reactions are well known to the skilled worker and described, for example, in  
10 "Surfactants in Consumer Products" (J. Falbe, Springer Verlag Heidelberg, 1987 and literature cited therein) or J. March, Advanced Organic Chemistry, 4th Edition, John Wiley & Sons, New York, 1992.

The epoxides of the formula (I') can be obtained by known methods, for example  
15 from the corresponding alkenes, and are commercially available, for example ethylene oxide or propylene oxide.

The compounds of the formula (I'') are commercially available and described in the literature; likewise, they can be prepared by standard reactions with which the skilled  
20 worker is familiar. Thus, for example, hydroxyaromatics, e.g. phenol, can be reacted with alcohols, olefins or alkyl halides under catalytic conditions (protic acids such as sulfuric or phosphoric acid, or Lewis acids such as aluminum chloride or boron trifluoride diethyl ether) to give the compounds of the formula (I''). A broad overview can be found in, for example, "Methoden der organischen Chemie" [Methods in  
25 organic chemistry] (Houben-Weyl), 4th Edition, 1976, Vol. 6/1c, p. 925 et seq.; (ISBN 3-13-204204-8).

Preferred surfactants are those of the formula (I) where Ar in formula (I) is a naphthyl or phenyl radical which has 3 to 7, preferably 3 to 5,  $(C_1-C_{10})$ alkyl radicals attached  
30 to it. Ar is preferably a phenyl radical which has 3 to 5  $(C_1-C_{10})$ alkyl radicals attached to it, such as tri( $C_1-C_6$ )alkylphenyl, especially preferably tributylphenyl such as tri-2,4,6-sec-butylphenyl.

R<sup>1</sup> and R<sup>2</sup> are preferably H or methyl, especially preferably H.

R<sup>3</sup> is preferably H, (C<sub>1</sub>-C<sub>22</sub>)alkyl, (C<sub>2</sub>-C<sub>22</sub>)alkenyl, (C<sub>2</sub>-C<sub>22</sub>)alkynyl, an acyl radical such as CO-(C<sub>1</sub>-C<sub>30</sub>)alkyl, CO-(C<sub>2</sub>-C<sub>30</sub>)alkenyl, CO-(C<sub>2</sub>-C<sub>30</sub>)alkynyl, CO-(C<sub>1</sub>-

- 5 C<sub>30</sub>)alkoxy, CO-(C<sub>2</sub>-C<sub>30</sub>)alkenyloxy, CO-(C<sub>2</sub>-C<sub>30</sub>)alkynyloxy or COH, or a sulfonate radical such as SO<sub>3</sub>X where X is H or a cation, such as an inorganic cation, for example an alkali metal or alkaline earth metal cation such as Na, K or Mg, or an organic cation, for example a primary, secondary, tertiary or quaternary ammonium ion such as NH<sub>3</sub>CH<sub>3</sub>, NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>, NH(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> or N(CH<sub>3</sub>)<sub>4</sub>, or
- 10 a phosphonate radical such as (O)P(OR') (OR''), where R', R'' independently of one another are H or a cation such as an inorganic cation, for example an alkali metal or alkaline earth metal cation such as Na, K or Mg, or an organic cation, for example a primary, secondary, tertiary or quaternary ammonium such as NH<sub>3</sub>CH<sub>3</sub>, NH<sub>2</sub>(CH<sub>5</sub>)<sub>2</sub>, NH(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> or N(CH<sub>3</sub>)<sub>4</sub>, it also being possible for R', R'' to be Ar-O-(CHR<sup>1</sup>CHR<sup>2</sup>)<sub>y</sub>
- 15 where Ar, R<sup>1</sup>, R<sup>2</sup> and y are as defined in formula (I).

R<sup>3</sup> is especially preferably H, (C<sub>1</sub>-C<sub>6</sub>)alkyl or SO<sub>3</sub>M, where M is a cation.

Values of from 2 to 20 are preferred for y, with values of from 2 to 14 being especially preferred and values of from 2 to 9 very especially preferred.

- 20 Very especially preferred surfactants of the formula (I) are those where Ar is tri(C<sub>1</sub>-C<sub>6</sub>)alkylphenyl, especially preferably tributylphenyl such as tri-2,4,6-sec-butylphenyl, R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = H and y is an integer of from 2 to 14, for example surfactants from the Sapogenat® T series by Clariant, for example Sapogenat® T 040, Sapogenat®
- 25 T 060, Sapogenat® T 070, Sapogenat® T 080, Sapogenat® T 090, Sapogenat® T 100, Sapogenat® T 110 and Sapogenat® T 130. Preferred as component a) are also mixtures of two or more different surfactants of the formula (I), for example of two or more different surfactants from the Sapogenat® T series.
- 30 In formula (I) and all other formulae of the present description, carbon-containing radicals such as alkyl, alkoxy, haloalkyl, haloalkoxy, alkylamino and alkylthio and the corresponding unsaturated and/or substituted radicals can be in each case straight-

chain or branched in the carbon skeleton. Unless specifically stated, these radicals generally have 1 to 30 carbon atoms, the lower carbon skeletons, for example those having 1 to 6 carbon atoms or, in the case of unsaturated groups, those having 2 to 6 carbon atoms, being preferred. Alkyl radicals, also in the composite meanings such

- 5 as alkoxy, haloalkyl and the like, are, for example, methyl, ethyl, n- or i-propyl, n-, i-, t- or sec-butyl, pentyl radicals, hexyl radicals such as n-hexyl, i-hexyl and 1,3-dimethylbutyl, heptyl radicals, such as n-heptyl, 1-methylhexyl and 1,4-dimethylpentyl; alkenyl and alkynyl radicals have the meanings of the possible unsaturated radicals which correspond to the alkyl radicals; alkenyl is, for example,
- 10 allyl, 1-methylprop-2-en-1-yl, 2-methylprop-2-en-1-yl, but-2-en-1-yl, but-3-en-1-yl, 1-methylbut-3-en-1-yl and 1-methylbut-2-en-1-yl; alkynyl is, for example, propargyl, but-2-yn-1-yl, but-3-yn-1-yl, 1-methylbut-3-yn-1-yl.

Alkenyl in the form  $(C_3-C_4)$ alkenyl,  $(C_3-C_5)$ alkenyl,  $(C_3-C_6)$ alkenyl,  $(C_3-C_8)$ alkenyl or

- 15  $(C_3-C_{12})$ alkenyl is preferably an alkenyl radical having 3 to 4, 3 to 5, 3 to 6, 3 to 8 and 3 to 12 carbon atoms, respectively, where the double bond is not located at the carbon atom which is linked to the remaining moiety of the compound of the formula (I) ("yl" position). This also applies analogously to  $(C_3-C_4)$ alkynyl and the like,  $(C_3-C_4)$ alkenyloxy and the like and  $(C_3-C_4)$ alkynyloxy and the like.

20

A hydrocarbon radical means a straight-chain, branched or cyclic and saturated or unsaturated aliphatic or aromatic hydrocarbon radical, for example alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl or aryl.

- A hydrocarbon radical has preferably 1 to 40 carbon atoms, preferably 1 to 30  
25 carbon atoms; a hydrocarbon radical is especially preferably alkyl, alkenyl or alkynyl having up to 12 carbon atoms or cycloalkyl having 3, 4, 5, 6 or 7 ring atoms, or phenyl.

- 30 Aryl is a mono-, bi- or polycyclic aromatic system, for example phenyl, naphthyl, tetrahydronaphthyl, indenyl, indanyl, pentalenyl, fluorenyl and the like, preferably phenyl.

A heterocyclic radical or ring (heterocyclyl) can be saturated, unsaturated or heteroaromatic and unsubstituted or substituted; preferably, it contains one or more hetero atoms in the ring, preferably selected from the group consisting of N, O and S; it is preferably an aliphatic heterocyclyl radical having 3 to 7 ring atoms or a

- 5 heteroaromatic radical having 5 or 6 ring atoms and contains 1, 2 or 3 hetero atoms. The heterocyclic radical can be, for example, a heteroaromatic radical or ring (heteroaryl) such as, for example, a mono-, bi- or polycyclic aromatic system in which at least 1 ring contains one or more hetero atoms, for example pyridyl, pyrimidinyl, pyridazinyl, pyrazinyl, triazinyl, thienyl, thiazolyl, oxazolyl, furyl, pyrrolyl,
- 10 pyrazolyl and imidazolyl, or a partially or fully hydrogenated radical such as oxiranyl, oxetanyl, pyrrolidyl, piperidyl, piperazinyl, dioxolanyl, morpholinyl, tetrahydrofuryl. Suitable substituents for a substituted heterocyclic radical are those substituents which are mentioned hereinbelow, and additionally oxo. The oxo group may also occur on those hetero ring atoms which may exist in different oxidation states, for
- 15 example N and S.

Halogen is, preferably, fluorine, chlorine, bromine or iodine. Haloalkyl, -alkenyl and -alkynyl are alkyl, alkenyl or alkynyl which are substituted in part or fully by halogen, preferably by fluorine, chlorine and/or bromine, in particular by fluorine or chlorine, e.g. CF<sub>3</sub>, CHF<sub>2</sub>, CH<sub>2</sub>F, CF<sub>3</sub>CF<sub>2</sub>, CH<sub>2</sub>FCHCl, CCl<sub>3</sub>, CHCl<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>Cl; haloalkoxy is, for example, OCF<sub>3</sub>, OCHF<sub>2</sub>, OCH<sub>2</sub>F, CF<sub>3</sub>CF<sub>2</sub>O, OCH<sub>2</sub>CF<sub>3</sub> and OCH<sub>2</sub>CH<sub>2</sub>Cl; this also applies analogously to haloalkenyl and other halogen-substituted radicals.

- Substituted radicals such as substituted hydrocarbon radicals, e.g. substituted alkyl, alkenyl, alkynyl, aryl, phenyl and benzyl, or substituted heterocyclyl or heteroaryl, are, for example, a substituted radical which is derived from the unsubstituted skeleton, where the substituents are, for example, one or more, preferably 1, 2 or 3, radicals selected from the group consisting of halogen, alkoxy, haloalkoxy, alkylthio, hydroxyl, amino, nitro, carboxyl, cyano, azido, alkoxy carbonyl, alkyl carbonyl, formyl, carbamoyl, mono- and dialkylaminocarbonyl, substituted amino such as acylamino, mono- and dialkylamino, and alkylsulfinyl, haloalkylsulfinyl, alkylsulfonyl, haloalkylsulfonyl and, in the case of cyclic radicals, also alkyl and haloalkyl, and

unsaturated aliphatic radicals which correspond to the abovementioned saturated hydrocarbon-containing radicals, such as alkenyl, alkynyl, alkenyloxy, alkynyloxy and the like. In the case of radicals with carbon atoms, those having 1 to 4 carbon atoms, in particular 1 or 2 carbon atoms, are preferred. Preferred substituents are, as a rule,

- 5 those from the group consisting of halogen, for example fluorine and chlorine, ( $C_1-C_4$ )alkyl, preferably methyl or ethyl, ( $C_1-C_4$ )haloalkyl, preferably trifluoromethyl, ( $C_1-C_4$ )alkoxy, preferably methoxy or ethoxy, ( $C_1-C_4$ )haloalkoxy, nitro and cyano. Especially preferred in this context are the substituents methyl, methoxy and chlorine.

10

Optionally substituted phenyl is preferably phenyl which is unsubstituted or mono- or polysubstituted, preferably up to trisubstituted, by identical or different radicals selected from the group consisting of halogen, ( $C_1-C_4$ )alkyl, ( $C_1-C_4$ )alkoxy, ( $C_1-C_4$ )haloalkyl, ( $C_1-C_4$ )haloalkoxy and nitro, for example o-, m- and p-tolyl, 15 dimethylphenyl radicals, 2-, 3- and 4-chlorophenyl, 2-, 3- and 4-trifluoro- and -trichlorophenyl, 2,4-, 3,5-, 2,5- and 2,3-dichlorophenyl, o-, m- and p-methoxyphenyl, 2,4,6-tributylphenyl such as 2,4,6-tri-sec-butylphenyl.

An acyl radical refers to the radical of an organic acid which is formed formally by 20 removing an OH group from the organic acid, for example the radical of a carboxylic acid and radicals of acids derived therefrom, such as thiocarboxylic acid, unsubstituted or N-substituted iminocarboxylic acids or the radicals of carbonic monoesters, unsubstituted or N-substituted carbamic acids, sulfonic acids, sulfinic acids, phosphonic acids, phosphinic acids.

25

An acyl radical is preferably formyl or aliphatic acyl selected from the group consisting of  $CO-R^x$ ,  $CS-R^x$ ,  $CO-OR^x$ ,  $CS-OR^x$ ,  $CS-SR^x$ ,  $SOR^Y$  or  $SO_2R^Y$ , where  $R^x$  and  $R^Y$  each are a  $C_1-C_{30}$  hydrocarbon radical which is unsubstituted or substituted, or aminocarbonyl or aminosulfonyl, the last-mentioned two radicals being 30 unsubstituted, N-monosubstituted or N,N-disubstituted.

Acyl is, for example, formyl, haloalkylcarbonyl, alkylcarbonyl such as ( $C_1-C_4$ )alkylcarbonyl, phenylcarbonyl, it being possible for the phenyl ring to be

substituted for example as stated above for phenyl, or is alkyloxycarbonyl, phenoxy carbonyl, benzyloxy carbonyl, alkylsulfonyl, alkylsulfinyl, N-alkyl-1-iminoalkyl and other radicals of organic acids.

- 5 Formula (I) and the other formulae in the present description also encompass all the stereoisomers and their mixtures. Such compounds contain one or more asymmetric carbon atoms or else double bonds which are not stated separately in the general formula. The possible stereoisomers, which are defined by their specific spatial form, such as enantiomers, diastereomers, Z and E isomers, are all embraced by the  
10 formulae in question and can be obtained by customary methods from mixtures of the stereoisomers or else by stereoselective reactions in combination with the use of stereochemically pure starting materials.

- The fatty acid esters which are present in the adjuvants according to the invention  
15 can be for example of natural origin, for example they can be natural oils such as animal oils or vegetable oils, or of synthetic origin, for example the Edenor® series, e.g. Edenor®MEPa or Edenor®MESU or the AGNIQUE®ME series or the AGNIQUE®AE series (Cognis), SALIM®ME series (Salim), Radia® series, e.g. Radia®30167 (Fina Chemicals), Priolube® series, e.g. Priolube®1530 (Unichema),  
20 STEPAN®C series (Stepan) or WITCONOL®23 series (Witco). The fatty acid esters are preferably esters of C<sub>10</sub>-C<sub>22</sub> fatty acids, preferably C<sub>12</sub>-C<sub>20</sub> fatty acids. The C<sub>10</sub>-C<sub>22</sub> fatty acid esters are, for example, esters of unsaturated or saturated C<sub>10</sub>-C<sub>22</sub> fatty acids, in particular those with an even number of carbon atoms, for example erucic acid, lauric acid, palmitic acid and, in particular, C<sub>18</sub> fatty acids such as stearic acid,  
25 oleic acid, linoleic acid or linolenic acid.

- Examples of fatty acid esters such as C<sub>10</sub>-C<sub>22</sub>fatty acid esters are glycerol and glycol esters of fatty acids such as C<sub>10</sub>-C<sub>22</sub>fatty acids or their transesterification products, for example alkyl fatty acid esters such as C<sub>1</sub>-C<sub>20</sub>alkyl C<sub>10</sub>-C<sub>22</sub>fatty acid esters as can  
30 be obtained, for example, by transesterification of the abovementioned glycerol or glycol fatty acid esters, such as C<sub>10</sub>-C<sub>22</sub>fatty acid esters, with C<sub>1</sub>-C<sub>20</sub>alcohols (for example methanol, ethanol, propanol or butanol). The transesterification reaction

can be carried out by known methods as are described, for example, in Römpf Chemie Lexikon [Römpf's dictionary of chemistry], 9th Edition, Volume 2, page 1343, Thieme Verlag Stuttgart.

- 5 Preferred alkyl fatty acid esters, such as C<sub>1</sub>-C<sub>20</sub>alkyl C<sub>10</sub>-C<sub>22</sub>fatty acid esters, are methyl esters, ethyl esters, propyl esters, butyl esters, 2-ethylhexyl esters and dodecyl esters. Preferred glycol and glycerol fatty acid esters, such as C<sub>10</sub>-C<sub>22</sub>fatty acid esters, are the uniform or mixed glycol esters and glycerol esters of C<sub>10</sub>-C<sub>22</sub>fatty acids, in particular those fatty acids with an even number of carbon atoms, for  
10 example erucic acid, lauric acid, palmitic acid and, in particular, C<sub>18</sub>fatty acids such as stearic acid, oleic acid, linoleic acid or linolenic acid.

Animal oils b) which are present in the adjuvants according to the invention are generally known and commercially available. For the purposes of the present  
15 invention, the term animal oils is understood as meaning, for example, oils of animal origin such as whale oil, cod-liver oil, musk oil or mink oil.

Vegetable oils b) which are present in the adjuvants according to the invention are generally known and commercially available. For the purposes of the present  
20 invention, the term vegetable oils is understood as meaning, for example, oils from oil-yielding plant species such as soya oil, rapeseed oil, corn oil, sunflower oil, cottonseed oil, linseed oil, coconut oil, palm oil, safflower oil, walnut oil, peanut oil, olive oil or castor oil, in particular rapeseed oil, the vegetable oils also meaning to include their transesterification products, for example alkyl esters such as rapeseed  
25 oil methyl ester or rapeseed oil ethyl ester.

The vegetable oils are preferably esters of C<sub>10</sub>-C<sub>22</sub>fatty acids, preferably C<sub>12</sub>-C<sub>20</sub>fatty acids. The C<sub>10</sub>-C<sub>22</sub>fatty acid esters are, for example, esters of unsaturated or saturated C<sub>10</sub>-C<sub>22</sub>fatty acids, in particular those with an even number of carbon  
30 atoms, for example erucic acid, lauric acid, palmitic acid and in particular C<sub>18</sub>fatty acids such as stearic acid, oleic acid, linoleic acid or linolenic acid.

- Examples of vegetable oils are C<sub>10</sub>-C<sub>22</sub>fatty acid esters of glycerol or glycol with the C<sub>10</sub>-C<sub>22</sub>fatty acids, or C<sub>1</sub>-C<sub>20</sub>alkyl C<sub>10</sub>-C<sub>22</sub>fatty acid esters, as they can be obtained, for example, by transesterification of the abovementioned glycerol or glycol C<sub>10</sub>-C<sub>22</sub>fatty acid esters with C<sub>1</sub>-C<sub>20</sub>alcohols (for example methanol, ethanol, propanol or butanol). The transesterification reaction can be carried out by known methods as they are described, for example, in Römpf Chemie Lexikon, 9th Edition, Volume 2, page 1343, Thieme Verlag Stuttgart.

The vegetable oils may be present in the adjuvants according to the invention for example in the form of commercially available vegetable oils, in particular rapeseed oils such as rapeseed oil methyl ester, for example Phytorob®B (Novance, France, hereinbelow referred to as Phytorob B), Edenor® MESU (Cognis, Germany, hereinbelow referred to as Edenor) and the Agnique® ME series (Cognis, Germany, hereinbelow referred to as Agnique), the Priolube® series (Unichema, hereinbelow referred to as Priolube) or Biodiesel, or in the form of commercially available formulation additives comprising vegetable oils, in particular those based on rapeseed oils such as rapeseed oil methyl ester, for example Hasten® (Victorian Chemical Company, Australia, hereinbelow referred to as Hasten, main constituent: rapeseed oil methyl ester), Actirob®B (Novance, France, hereinbelow referred to as ActirobB, main constituent: rapeseed oil methyl ester), Rako-Binol® (Bayer AG, Germany, hereinbelow referred to as Rako-Binol, main constituent: rapeseed oil), Renol® (Stefes, Germany, hereinbelow referred to as Renol, vegetable oil constituent: rapeseed oil methyl ester) or Stefes Mero® (Stefes, Germany, hereinbelow referred to as Mero, main constituent: rapeseed oil methyl ester).

25

Examples of synthetic fatty acid esters are, for example, those which are derived from fatty acids with an odd number of carbon atoms, such as C<sub>11</sub>-C<sub>21</sub>fatty acid esters.

30 The adjuvants according to the invention are liquid under standard conditions (atmospheric pressure, room temperature). In general, they comprise between 1 and 50% by weight, preferably between 2 and 30% by weight, particularly preferably

between 2 and 20% by weight, of one or more surfactants of the formula (I), and between 99 and 50% by weight, preferably between 98 and 70% by weight, particularly preferably between 98 and 80% by weight, of one or more fatty acid esters b), such as vegetable oils. The content may also be lower or higher than 5 these limits in individual cases. Preferred adjuvants according to the invention comprise the fatty acid esters b), such as vegetable oils, in an excess in comparison with the surfactants of the formula (I).

In addition, the adjuvants according to the invention may comprise typical auxiliaires 10 such as additives and formulation aids. The term auxiliaries is understood as meaning materials which are largely inert chemically and biologically, and whose use allows a composition to be handled as intended.

Examples of auxiliaries are

- 15 • wetting agents such as Genapol® LRO (0-20% by weight), dispersants such as Tamol® (0-15% by weight) or other surfactants (nonionic, cationic, anionic, polymeric surfactants) (0-30% by weight);
- inorganic salts such as NaCl, MgCl<sub>2</sub> (0-50% by weight), (oligo-, poly-)phosphates;
- fertilizers such as ammonium sulfate, ammonium nitrate, urea, phosphorus- and 20 potassium-containing components, if desired other trace elements (0-60% by weight);
- antifoams, for example silicone-based antifoams, such as SE2® (Wacker Chemie) or Silolapse®5020 (Rhodia) (0-2% by weight);
- binders such as suitable natural or synthetic materials, such as polyamino acids,
- 25 polyvinyl alcohols, polyvinylpyrrolidone, polyacrylic acid derivatives (0-15% by weight); or
- solvents such as water or organic solvents (0-15% by weight).

The amounts (% by weight) stated for the auxiliaries are ranges which are to be 30 regarded as typical, but which may also be lower or higher in individual cases.

The adjuvants according to the invention are prepared by customary methods, for example mixing by dissolving or emulsifying the individual components, preferably at room temperature. If other auxiliaries are present, they are likewise incorporated at, preferably, room temperature. In general, the sequence in which the individual

5 components are added is of no importance.

The adjuvants according to the invention can be combined with one or more agrochemical active substances c) to give agrochemical compositions, for example in the form of coformulations or tank mixes, preferably tank mixes. Such

10 agrochemical compositions are likewise novel and subject of the present invention.

Examples of suitable agrochemical active substances are herbicides, insecticides, fungicides, safeners and growth regulators. Preferred agrochemical active substances are herbicides, for example foliar-acting herbicides such as ALS

15 inhibitors (for example sulfonamides such as flucarbazone, propoxycarbazone or amicarbazone, or sulfonylureas such as mesosulfuron, ethoxysulfuron, iodosulfuron, amidosulfuron, foramsulfuron), diflufenican, bromoxynil- or ioxynil-containing products, herbicides from the class of the aryloxyphenoxypropionates such as fenoxaprop-p-ethyl, sugarbeet herbicides such as desmedipham, phenmedipham,

20 ethofumesate or metamitron, glyphosate or glufosinate or else active substances from the class of the HPPD inhibitors (for example isoxaflutole, sulcotrione, mesotrione).

Herbicides which are present in the agrochemical compositions according to the

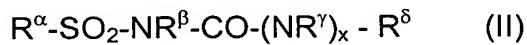
25 invention are, for example, ALS inhibitors (acetolactate synthetase inhibitors), or herbicides other than ALS inhibitors, such as herbicides from the group of the carbamates, thiocarbamates, haloacetanilides, substituted phenoxy-, naphthoxy- and phenoxyphenoxycarboxylic acid derivatives and

30 heteroaryloxyphenoxyalkanecarboxylic acid derivatives such as quinolyloxy-, quinoxalyloxy-, pyridyloxy-, benzoxazolyloxy- and benzothiazolyloxyphenoxyalkanecarboxylic esters, cyclohexanedione derivatives, phosphorus-containing herbicides, for example herbicides of the glufosinate type or

of the glyphosate type, and S-(N-aryl-N-alkylcarbamoylmethyl)dithiophosphoric acid esters.

The ALS inhibitors are, in particular, imidazolinones, pyrimidinyloxypyridinecarboxylic

- 5 acid derivatives, pyrimidyloxybenzoic acid derivatives, triazolopyrimidinesulfonamide derivatives and sulfonamides, preferably from the group of the sulfonylureas, particularly preferably those of the general formula (II) and/or their salts,



10 where

$R^{\alpha}$  is a hydrocarbon radical, preferably an aryl radical such as phenyl, which is unsubstituted or substituted, or a heterocyclic radical, preferably a heteroaryl radical such as pyridyl, which is unsubstituted or substituted, and where the radicals including substituents have 1-30 carbon atoms, preferably 1-20 carbon atoms, or  $R^{\alpha}$  is an electron-attracting group such as a sulfonamide radical,

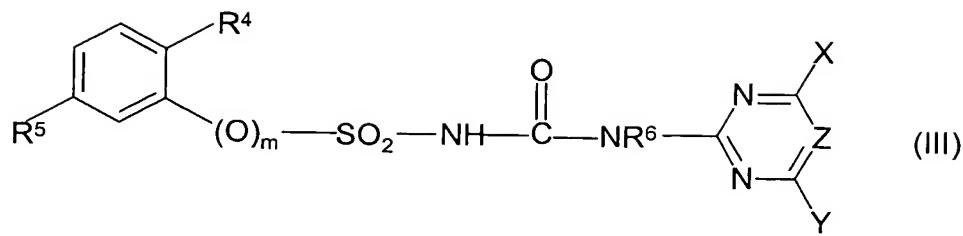
15  $R^{\beta}$  is a hydrogen atom or a hydrocarbon radical which is unsubstituted or substituted and, including substituents, has 1-10 carbon atoms, for example unsubstituted or substituted C<sub>1</sub>-C<sub>6</sub>alkyl, preferably a hydrogen atom or methyl,

20  $R^{\gamma}$  is a hydrogen atom or a hydrocarbon radical which is unsubstituted or substituted and, including substituents, has 1-10 carbon atoms, for example unsubstituted or substituted C<sub>1</sub>-C<sub>6</sub>alkyl, preferably a hydrogen atom or methyl,

$x$  is zero or 1, and

25  $R^{\delta}$  is a heterocyclic radical.

Especially preferred ALS inhibitors are sulfonylureas of the formula (III) and/or their salts,



where

$R^4$  is  $C_1\text{-}C_4$ alkoxy, preferably  $C_2\text{-}C_4$ alkoxy, or  $\text{CO}-R^a$  where  $R^a$  is OH,

5  $C_1\text{-}C_4$ alkoxy or  $\text{NR}^bR^c$ , where  $R^b$  and  $R^c$  independently of one another are identical or different and are H or  $C_1\text{-}C_4$ alkyl,

$R^5$  is halogen or  $(A)_n\text{-NR}^dR^e$  where n is zero or 1, A is a group  $\text{CR}'\text{R}''$  where  $R'$  and  $R''$  independently of one another are identical or different and are H or  $C_1\text{-}C_4$ alkyl,  $R^d$  is H or  $C_1\text{-}C_4$ alkyl and  $R^e$  is an acyl radical such as formyl or  $C_1\text{-}C_4$ alkylsulfonyl, and, in the event that  $R^4$  is  $C_1\text{-}C_4$ alkoxy, preferably  $C_2\text{-}C_4$ alkoxy,  $R^5$  may also be H,

10  $R^6$  is H or  $C_1\text{-}C_4$ alkyl,

$m$  is zero or 1, preferably zero,

X and Y independently of one another are identical or different and are  $C_1\text{-}C_6$ alkyl,  $C_1\text{-}C_6$ alkoxy or  $C_1\text{-}C_6$ alkylthio, where each of the three radicals mentioned is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen,  $C_1\text{-}C_4$ alkoxy and  $C_1\text{-}C_4$ alkylthio, or are  $C_3\text{-}C_6$ cycloalkyl,

15  $C_2\text{-}C_6$ alkenyl,  $C_2\text{-}C_6$ alkynyl,  $C_3\text{-}C_6$ alkenyloxy or  $C_3\text{-}C_6$ alkynyloxy, preferably  $C_1\text{-}C_4$ alkyl or  $C_1\text{-}C_4$ alkoxy, and

Z is CH or N.

20

Preferred sulfonylureas of the formula (III) and/or their salts are those in which

$m$  is zero and

- 25 a)  $R^4$  is  $\text{CO-(}C_1\text{-}C_4\text{alkoxy)}$  and  $R^5$  is halogen, preferably iodine, or  $R^5$  is  $\text{CH}_2\text{-NHR}^e$  where  $R^e$  is an acyl radical, preferably  $C_1\text{-}C_4$ -alkylsulfonyl, or  
 b)  $R^4$  is  $\text{CO-N(C}_1\text{-}C_4\text{alkyl)}_2$  and  $R^5$  is  $\text{NHR}^e$  where  $R^e$  is an acyl radical, preferably formyl.

For the purposes of the present invention, the active substances from the group of the ALS inhibitors, such as sulfonylureas, which are present as component in the herbicidal compositions according to the invention are always also understood as meaning not only the neutral compounds, but also their salts with inorganic and/or organic counterions. Thus, for example, sulfonylureas may form salts in which the hydrogen of the  $-\text{SO}_2\text{-NH-}$  group is replaced by an agriculturally suitable cation. Examples of these salts are metal salts, in particular alkali metal salts or alkaline earth metal salts, in particular sodium and potassium salts, or else ammonium salts or salts with organic amines. Likewise, salt formation may take place by addition of an acid to basic groups such as, for example, amino and alkylamino. Acids which are suitable for this purpose are strong inorganic and organic acids, for example HCl, HBr,  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$ .

Preferred ALS inhibitors are from the series of the sulfonylureas, for example pyrimidine- or triazinylaminocarbonyl[benzene-, pyridine-, pyrazole-, thiophene- and (alkylsulfonyl)alkylamino]sulfamides. Preferred as substituents on the pyrimidine ring or triazine ring are alkoxy, alkyl, haloalkoxy, haloalkyl, halogen or dimethylamino, it being possible for all substituents to be combined independently of one another. Preferred substituents in the benzene-, pyridine-, pyrazole-, thiophene- or (alkylsulfonyl)alkylamino moiety are alkyl, alkoxy, halogen such as F, Cl, Br or I, amino, alkylamino, dialkylamino, acylamino such as formylamino, nitro, alkoxycarbonyl, aminocarbonyl, alkylaminocarbonyl, dialkylaminocarbonyl, alkoxyaminocarbonyl, haloalkoxy, haloalkyl, alkylcarbonyl, alkoxyalkyl, alkylsulfonylaminooalkyl, (alkanesulfonyl)alkylamino. Examples of such suitable sulfonylureas are

- A1) Phenyl- and benzylsulfonylureas and related compounds, for example 1-(2-chlorophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (chlorsulfuron),
- 30 1-(2-ethoxycarbonylphenylsulfonyl)-3-(4-chloro-6-methoxypyrimidin-2-yl)urea (chlorimuron-ethyl),

- 1-(2-methoxyphenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea  
(metsulfuron-methyl),  
1-(2-chloroethoxyphenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea  
(triasulfuron),  
5 1-(2-methoxycarbonylphenylsulfonyl)-3-(4,6-dimethylpyrimidin-2-yl)urea  
(sulfometuron-methyl),  
1-(2-methoxycarbonylphenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-3-  
methylurea (tribenuron-methyl),  
1-(2-methoxycarbonylbenzylsulfonyl)-3-(4,6-dimethoxypyrimidin-2-yl)urea  
10 (bensulfuron-methyl),  
1-(2-methoxycarbonylphenylsulfonyl)-3-(4,6-bis(difluoromethoxy)pyrimidin-2-yl)urea,  
(primisulfuron-methyl),  
3-(4-ethyl-6-methoxy-1,3,5-triazin-2-yl)-1-(2,3-dihydro-1,1-dioxo-2-methylbenzo-  
[b]thiophen-7-sulfonyl)urea (EP-A 0 796 83),  
15 3-(4-ethoxy-6-ethyl-1,3,5-triazin-2-yl)-1-(2,3-dihydro-1,1-dioxo-2-methylbenzo[b]-  
thiophen-7-sulfonyl)urea (EP-A 0 079 683),  
3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-1-(2-methoxycarbonyl-5-iodophenyl-  
sulfonyl)urea (idosulfuron-methyl and its salts such as the sodium salt, WO  
92/13845),  
20 DPX-66037, triflusulfuron-methyl (see Brighton Crop Prot. Conf. - Weeds - 1995, p.  
853),  
CGA-277476, (see Brighton Crop Prot. Conf. - Weeds - 1995, p. 79),  
methyl 2-[3-(4,6-dimethoxypyrimidin-2-yl)ureidosulfonyl]-4-methanesulfonamido-  
methylbenzoate (mesosulfuron-methyl and its salts such as the sodium salt, WO  
25 95/10507),  
N,N-dimethyl-2-[3-(4,6-dimethoxypyrimidin-2-yl)ureidosulfonyl]-4-formylamino-  
benzamide (foramsulfuron and its salts such as the sodium salt, WO 95/01344);
- A2) Thienylsulfonylureas, for example
- 30 1-(2-methoxycarbonylthiophen-3-yl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea  
(thifensulfuron-methyl);

A3) Pyrazolylsulfonylureas, for example

1-(4-ethoxycarbonyl-1-methylpyrazol-5-ylsulfonyl)-3-(4,6-dimethoxypyrimidin-2-yl)urea (pyrazosulfuron-methyl);  
 methyl 3-chloro-5-(4,6-dimethoxypyrimidin-2-ylcarbamoylsulfamoyl)-1-methyl-  
 5 pyrazole-4-carboxylate (EP-A 0 282 613);  
 methyl 5-(4,6-dimethylpyrimidin-2-ylcarbamoylsulfamoyl)-1-(2-pyridyl)pyrazole-4-  
 carboxylate (NC-330, see Brighton Crop Prot. Conference 'Weeds' 1991, Vol. 1, p.  
 45 et seq.),  
 DPX-A8947, azimsulfuron, (see Brighton Crop Prot. Conf. 'Weeds' 1995, p. 65);

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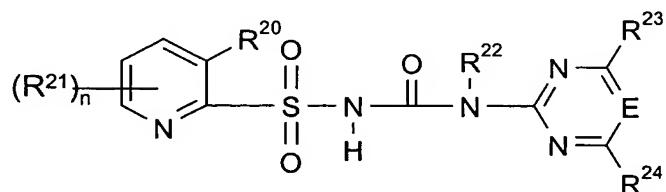
A4) Sulfonediamide derivatives, for example

3-(4,6-dimethoxypyrimidin-2-yl)-1-(N-methyl-N-methylsulfonylaminosulfonyl)urea  
 (amidosulfuron) and its structural analogs (EP-A 0 131 258 and Z. Pfl. Krankh. Pfl.  
 Schutz, Special Issue XII, 489-497 (1990));

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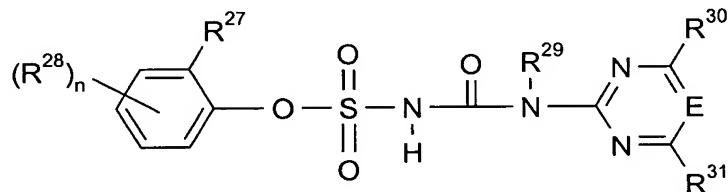
A5) Pyridylsulfonylureas, for example

1-(3-N,N-dimethylaminocarbonylpyridin-2-ylsulfonyl)-3-(4,6-dimethoxypyrimidin-2-yl)urea (nicosulfuron),  
 1-(3-ethylsulfonylpyridin-2-ylsulfonyl)-3-(4,6-dimethoxypyrimidin-2-yl)urea  
 (rimsulfuron),  
 methyl 2-[3-(4,6-dimethoxypyrimidin-2-yl)ureidosulfonyl]-6-trifluoromethyl-3-pyridine-  
 carboxylate, sodium salt (DPX-KE 459, flupyralsulfuron, see Brighton Crop Prot. Conf.  
 Weeds, 1995, p. 49),  
 pyridylsulfonylureas as are described, for example in DE-A 40 00 503 and DE-  
 25 A 40 30 577, preferably those of the formula



in which

- E is CH or N, preferably CH,  
 $R^{20}$  is iodine or  $NR^{25}R^{26}$ ,  
 $R^{21}$  is hydrogen, halogen, cyano, ( $C_1-C_3$ )alkyl, ( $C_1-C_3$ )alkoxy, ( $C_1-C_3$ )haloalkyl, ( $C_1-C_3$ )haloalkoxy, ( $C_1-C_3$ )alkylthio, ( $C_1-C_3$ )alkoxy( $C_1-C_3$ )alkyl, ( $C_1-C_3$ )-alkoxycarbonyl, mono- or di(( $C_1-C_3$ )alkyl)amino, ( $C_1-C_3$ )alkylsulfinyl or -sulfonyl,  $SO_2-NR^X R^Y$  or  $CO-NR^X R^Y$ , in particular hydrogen,  
5  $R^X, R^Y$  independently of one another are hydrogen, ( $C_1-C_3$ )alkyl, ( $C_1-C_3$ )alkenyl, ( $C_1-C_3$ )alkynyl or together are  $-(CH_2)_4-$ ,  $-(CH_2)_5-$  or  $-(CH_2)_2-O-(CH_2)_2-$ ,  
n is 0,1,2 or 3, preferably 0 or 1,  
10  $R^{22}$  is hydrogen or  $CH_3$ ,  
 $R^{23}$  is halogen, ( $C_1-C_2$ )alkyl, ( $C_1-C_2$ )alkoxy, ( $C_1-C_2$ )haloalkyl, in particular  $CF_3$ , ( $C_1-C_2$ )haloalkoxy, preferably  $OCHF_2$  or  $OCH_2CF_3$ ,  
 $R^{24}$  is ( $C_1-C_2$ )alkyl, ( $C_1-C_2$ )haloalkoxy, preferably  $OCHF_2$ , or ( $C_1-C_2$ )alkoxy,  
 $R^{25}$  is ( $C_1-C_4$ )alkyl,  
15  $R^{26}$  is ( $C_1-C_4$ )alkylsulfonyl or  
 $R^{25}$  and  $R^{26}$  together are a chain of the formula  $-(CH_2)_3SO_2-$  or  $-(CH_2)_4SO_2-$ , for example 3-(4,6-dimethoxypyrimiden-2-yl)-1-(3-N-methylsulfonyl-N-methylaminopyridin-2-yl)sulfonylurea, or their salts;
- 20 A6) Alkoxyphenoxy sulfonyleureas as are described, for example, in EP-A 0 342 569, preferably those of the formula



in which

- 25 E is CH or N, preferably CH,  
 $R^{27}$  is ethoxy, propoxy or isopropoxy,  
 $R^{28}$  is halogen,  $NO_2$ ,  $CF_3$ ,  $CN$ , ( $C_1-C_4$ )alkyl, ( $C_1-C_4$ )alkoxy, ( $C_1-C_4$ )alkylthio or ( $C_1-C_3$ )alkoxycarbonyl, preferably in the 6-position on the phenyl ring,  
n is 0, 1, 2 or 3, preferably 0 or 1,

R<sup>29</sup> is hydrogen, (C<sub>1</sub>-C<sub>4</sub>)alkyl or (C<sub>3</sub>-C<sub>4</sub>)alkenyl,

R<sup>30</sup>, R<sup>31</sup> independently of one another are halogen, (C<sub>1</sub>-C<sub>2</sub>)alkyl, (C<sub>1</sub>-C<sub>2</sub>)alkoxy, (C<sub>1</sub>-C<sub>2</sub>)haloalkyl, (C<sub>1</sub>-C<sub>2</sub>)haloalkoxy or (C<sub>1</sub>-C<sub>2</sub>)alkoxy(C<sub>1</sub>-C<sub>2</sub>)alkyl, preferably OCH<sub>3</sub> or CH<sub>3</sub>, for example 3-(4,6-dimethoxypyrimidin-2-yl)-1-(2-

5 ethoxyphenoxy)sulfonylurea, or their salts;

A7) Imidazolylsulfonylureas, for example

MON 37500, sulfosulfuron (see Brighton Crop Prot. Conf. 'Weeds', 1995, p. 57), and other related sulfonylurea derivatives and mixtures of these.

10

Typical representatives of these active substances are, inter alia, the compounds listed hereinbelow: amidosulfuron, azimsulfuron, bensulfuron-methyl, chlorimuron-ethyl, chlorsulfuron, cinosulfuron, cyclosulfamuron, ethametsulfuron-methyl, ethoxysulfuron and its sodium salt, flazasulfuron, flupyralsulfuron-methyl-sodium,

15 halosulfuron-methyl, imazosulfuron, metsulfuron-methyl, nicosulfuron, oxasulfuron, primisulfuron-methyl, prosulfuron, pyrazosulfuron-ethyl, rimsulfuron, sulfometuron-methyl, sulfosulfuron, thifensulfuron-methyl, triasulfuron, tribenuron-methyl, triflusulfuron-methyl, iodosulfuron-methyl and its sodium salt (WO 92/13845), mesosulfuron-methyl and its sodium salt (Agrow No. 347, March 3, 2000, page 22

20 (PJB Publications Ltd. 2000)) and forumsulfuron and its sodium salt (Agrow No. 338, October 15, 1999, page 26 (PJB Publications Ltd. 1999)).

The active substances listed hereinabove are known, for example, from "The Pesticide Manual", 12<sup>th</sup> Edition (2000), The British Crop Protection Council, or the references cited after the individual active substances.

25 Other suitable ALS inhibitors are, for example

B) Imidazolinones, for example

30 methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-5-methylbenzoate and 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-4-methylbenzoic acid (imazamethabenz),

- 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)pyridine-3-carboxylic acid (imazethapyr),  
2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)quinoline-3-carboxylic acid (imazaquin),
- 5 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)pyridine-3-carboxylic acid (imazapyr),  
5-methyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)pyridine-3-carboxylic acid (imazethamethapyr);
- 10 C) Triazolopyrimidinesulfonamide derivatives, for example  
N-(2,6-difluorophenyl)-7-methyl-1,2,4-triazolo[1,5-c]pyrimidine-2-sulfonamide (flumetsulam),  
N-(2,6-dichloro-3-methylphenyl)-5,7-dimethoxy-1,2,4-triazolo[1,5-c]pyrimidine-2-sulfonamide,
- 15 N-(2,6-difluorophenyl)-7-fluoro-5-methoxy-1,2,4-triazolo[1,5-c]pyrimidine-2-sulfonamide,  
N-(2,6-dichloro-3-methylphenyl)-7-chloro-5-methoxy-1,2,4-triazolo[1,5-c]pyrimidine-2-sulfonamide,  
N-(2-chloro-6-methoxycarbonyl)-5,7-dimethyl-1,2,4-triazolo[1,5-c]pyrimidine-2-sulfonamide (EP-A 0 343 752, US-A 4,988,812);
- D) Pyrimidinyloxypyridinecarboxylic acid and pyrimidinyloxybenzoic acid derivatives, for example  
benzyl 3-(4,6-dimethoxypyrimidin-2-yl)oxygenypyridine-2-carboxylate (EP-A 0 249 707),
- 25 methyl 3-(4,6-dimethoxypyrimidin-2-yl)oxygenypyridine-2-carboxylate (EP-A 0 249 707),  
2,6-bis[(4,6-dimethoxypyrimidin-2-yl)oxygen]benzoic acid (EP-A 0 321 846),  
1-(ethoxycarbonyloxyethyl) 2,6-bis[(4,6-dimethoxypyrimidin-2-yl)oxygen]benzoate (EP-A 0 472 113).
- 30 The herbicidal active substances which are present in the herbicidal compositions according to the invention and which differ from the ALS inhibitors are, for example, herbicides from the group of the carbamates, thiocarbamates, haloacetanilides,

substituted phenoxy-, naphthoxy- and phenoxyphenoxy carboxylic acid derivatives, and heteroaryloxyphenoxy alkanecarboxylic acid derivatives such as quinolyloxy-, quinoxalyloxy-, pyridyloxy-, benzoxazolyloxy- and

benzothiazolyloxyphenoxy alkanecarboxylic esters, cyclohexanedione derivatives,

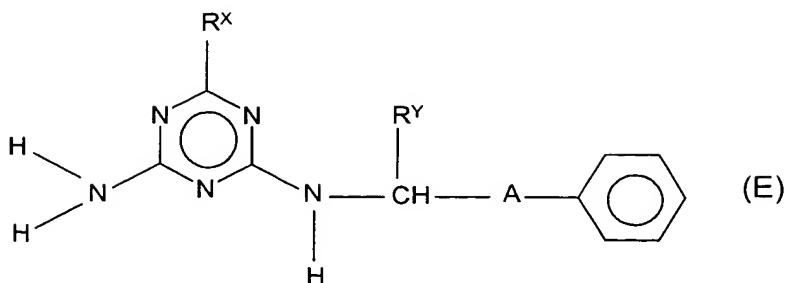
- 5 phosphorus-containing herbicides, for example of the glufosinate type or of the glyphosate type, and S-(N-aryl-N-alkylcarbamoylmethyl)dithiophosphoric esters. Preferred in this context are phenoxyphenoxy- and heteroaryloxyphenoxy carboxylic esters and their salts, and herbicides such as bentazone, cyanazine, atrazine, dicamba or hydroxybenzonitriles such as bromoxynil and ioxynil and other foliar-
- 10 acting herbicides.

Suitable herbicidal active substances which differ from the ALS inhibitors and which may be present as a component in the agrochemical compositions according to the invention are, for example:

- 15 E) Herbicides of the phenoxyphenoxy- and heteroaryloxyphenoxy carboxylic acid derivatives type, such as
- E1) Phenoxyphenoxy- and benzyloxyphenoxy carboxylic acid derivatives, for example methyl 2-(4-(2,4-dichlorophenoxy)phenoxy)propionate (diclofop-methyl),
- 20 methyl 2-(4-(4-bromo-2-chlorophenoxy)phenoxy)propionate (DE-A 26 01 548), methyl 2-(4-(4-bromo-2-fluorophenoxy)phenoxy)propionate (US-A 4,808,750), methyl 2-(4-(2-chloro-4-trifluoromethylphenoxy)phenoxy)propionate (DE-A 24 33 067), methyl 2-(4-(2-fluoro-4-trifluoromethylphenoxy)phenoxy)propionate (US-A 25 4,808,750), methyl 2-(4-(2,4-dichlorobenzyl)phenoxy)propionate (DE-A 24 17 487), ethyl 4-(4-(4-trifluoromethylphenoxy)phenoxy)pent-2-enoate, methyl 2-(4-(4-trifluoromethylphenoxy)phenoxy)propionate (DE-A 24 33 067);
- 30 E2) "Mononuclear" heteroaryloxyphenoxy alkanecarboxylic acid derivatives, for example ethyl 2-(4-(3,5-dichloropyridyl-2-oxy)phenoxy)propionate (EP-A 0 002 925),

- propargyl 2-(4-(3,5-dichloropyridyl-2-oxy)phenoxy)propionate (EP-A 0 003 114),  
methyl 2-(4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy)propionate  
(EP-A 0 003 890),  
ethyl 2-(4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy)propionate  
5 (EP-A 0 003 890),  
propargyl 2-(4-(5-chloro-3-fluoro-2-pyridyloxy)phenoxy)propionate (EP-A 0 191 736),  
butyl 2-(4-(5-trifluoromethyl-2-pyridyloxy)phenoxy)propionate  
(fluazifop-butyl);
- 10 E3) "Binuclear" heteroaryloxyphenoxyalkanecarboxylic acid derivatives, for example  
methyl and ethyl 2-(4-(6-chloro-2-quinoxalyloxy)phenoxy)propionate  
(quizalofopmethyl and quizalofopethyl),  
methyl 2-(4-(6-fluoro-2-quinoxalyloxy)phenoxy)propionate (see J. Pest. Sci. Vol. 10,  
15 61 (1985)),  
2-isopropylideneaminoxyethyl 2-(4-(6-chloro-2-quinoxalyloxy)phenoxy)propionate  
(propaquizafop),  
ethyl 2-(4-(6-chlorobenzoxazol-2-yloxy)phenoxy)propionate (fenoxaprop-ethyl), its  
D(+) isomer (fenoxaprop-P-ethyl) and ethyl 2-(4-(6-chlorobenzothiazol-2-  
20 yloxy)phenoxy)propionate (DE-A 26 40 730),  
tetrahydro-2-furylmethyl 2-(4-(6-chloroquinoxalyloxy)phenoxy)propionate (EP-A  
0 323 727);
- F) Chloracetanilides, for example  
25 N-methoxymethyl-2,6-diethylchloroacetanilide (alachlor),  
N-(3-methoxyprop-2-yl)-2-methyl-6-ethylchloroacetanilide (metolachlor),  
2,6-dimethyl-N-(3-methyl-1,2,4-oxadiazol-5-ylmethyl)chloroacetanilide,  
N-(2,6-dimethylphenyl)-N-(1-pyrazolylmethyl)chloroacetamide (metazachlor);
- 30 G) Thiocarbamates, for example  
S-ethyl N,N-dipropylthiocarbamate (EPTC),  
S-ethyl N,N-diisobutylthiocarbamate (butylate);

- H) Cyclohexanedione oximes, for example  
methyl 3-(1-allyloxyiminobutyl)-4-hydroxy-6,6-dimethyl-2-oxocyclohex-3-  
ene carboxylate (alloxydim),  
2-(1-ethoxyiminobutyl)-5-(2-ethylthiopropyl)-3-hydroxycyclohex-2-en-1-one  
5 (sethoxydim),  
2-(1-ethoxyiminobutyl)-5-(2-phenylthiopropyl)-3-hydroxycyclohex-2-en-1-one  
(cloproxydim),  
2-(1-(3-chloroallyloxy)iminobutyl)-5-(2-ethylthiopropyl)-3-hydroxycyclohex-2-en-1-  
one,  
10 2-(1-(3-chloroallyloxy)iminopropyl)-5-(2-ethylthiopropyl)-3-hydroxycyclohex-2-en-1-  
one (clethodim),  
2-(1-ethoxyiminobutyl)-3-hydroxy-5-(thian-3-yl)cyclohex-2-enone (cycloxydim),  
2-(1-ethoxyiminopropyl)-5-(2,4,6-trimethylphenyl)-3-hydroxycyclohex-2-en-1-one  
20 (tralkoxydim);  
15 I) Benzoylcyclohexanediones, for example  
2-(2-chloro-4-methylsulfonylbenzoyl)cyclohexane-1,3-dione (SC-0051, EP-A  
0 137 963, sulcotrione), 2-(2-nitrobenzoyl)-4,4-dimethylcyclohexane-1,3-dione (EP-A  
0 274 634), 2-(2-nitro-4-methylsulfonylbenzoyl)-4,4-dimethylcyclohexane-1,3-dione  
20 (WO 91/13548, mesotriione);  
J) S-(N-Aryl-N-alkylcarbamoylmethyl) dithiophosphonates such as S-[N-(4-  
chlorophenyl)-N-isopropylcarbamoylmethyl] O,O-dimethyl dithiophosphate  
(anilophos).  
25 K) Alkylazines, for example as described in WO-A 97/08156, WO-A-97/31904,  
DE-A-19826670, WO-A-98/15536, WO-A-98/15537, WO-A-98/15538, WO-A-  
98/15539 and also DE-A-19828519, WO-A-98/34925, WO-A-98/42684, WO-A-  
99/18100, WO-A-99/19309, WO-A-99/37627 and WO-A-99/65882, preferably those  
30 of the formula (E)

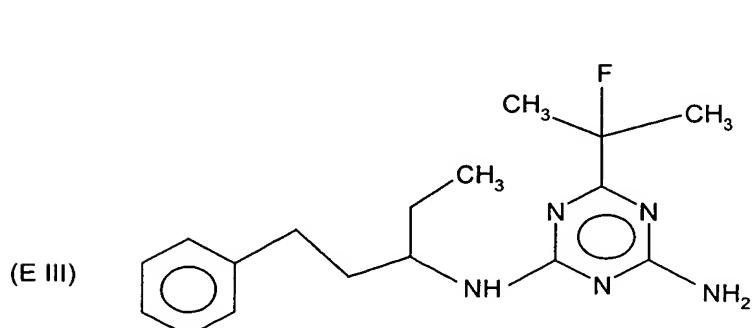
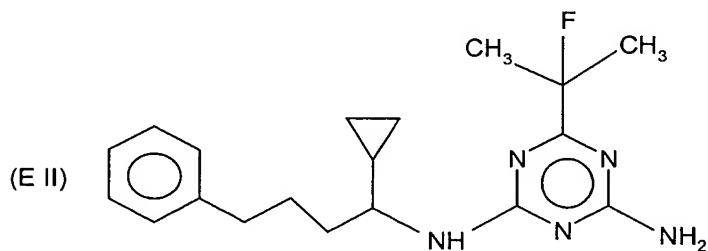
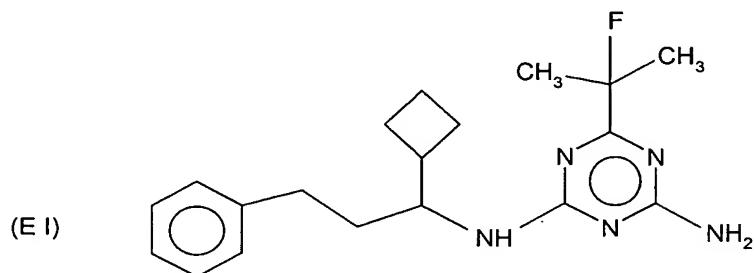


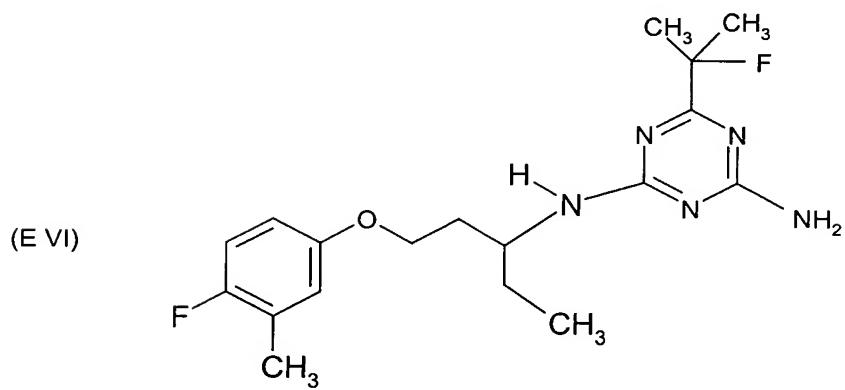
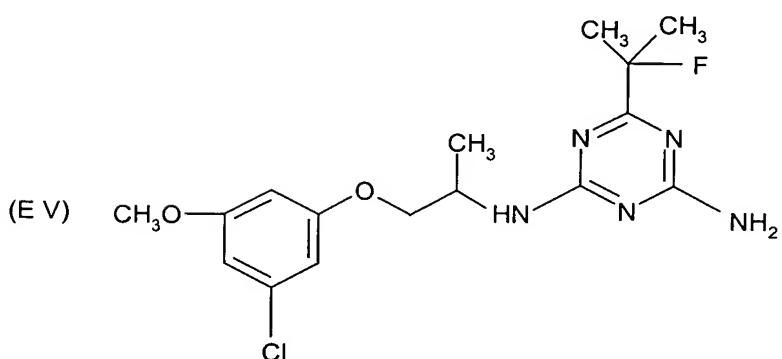
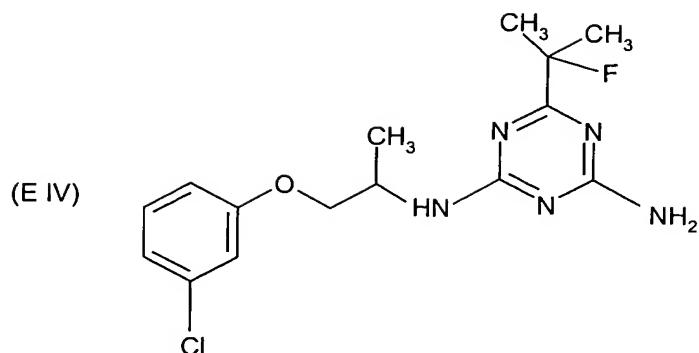
in which

$R^X$  is ( $C_1-C_4$ )alkyl or ( $C_1-C_4$ )haloalkyl;

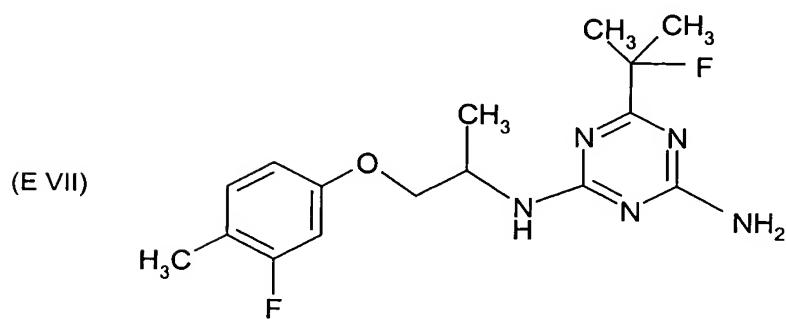
$R^Y$  is ( $C_1-C_4$ )alkyl, ( $C_3-C_6$ )cycloalkyl or ( $C_3-C_6$ )cycloalkyl( $C_1-C_4$ )alkyl and

- 5 A is  $-CH_2-$ ,  $-CH_2-CH_2-$ ,  $-CH_2-CH_2-CH_2-$ ,  $-O-$ ,  $-CH_2-CH_2-O-$ ,  $-CH_2-CH_2-CH_2-O-$ , especially preferably those of the formula E I-E VII





5



- L) Phosphorus-containing herbicides, for example of the glufosinate type, such as glufosinate in the narrow sense, i.e. D,L-2-amino-4-[hydroxy(methyl)phosphinyl]-butanoic acid, glufosinatemonoammonium salt, L-glufosinate, L- or (2S)-2-amino-4-[hydroxy(methyl)phosphinyl]butanoic acid, L-glufosinatemonoammonium salt or bialaphos (or bilanafos), i.e. L-2-amino-4-[hydroxy(methyl)phosphinyl]butanoyl-L-alanyl-L-alanine, in particular its sodium salt, or of the glyphosate type, such as glyphosate, i.e. N-(phosphonomethyl)glycine, glyphosatemonoisopropylammonium salt, glyphosate sodium salt, or sulfosate, i.e. N-(phosphonomethyl)glycine trimesium salt = N-(phosphonomethyl)glycine
- 5 10 trimethylsulfoxonium salt.

The herbicides of groups B to L are known, for example, from each of the specifications stated above and from "The Pesticide Manual", 12<sup>th</sup> Edition, 2000, The British Crop Protection Council, "Agricultural Chemicals Book II - Herbicides -", by

15 W.T. Thompson, Thompson Publications, Fresno CA, USA 1990 and "Farm Chemicals Handbook '90", Meister Publishing Company, Willoughby OH, USA, 1990.

Especially preferred herbicides are, for example, mesosulfuron and its salts and esters such as mesosulfuron-methyl and mesosulfuron-methyl-sodium (C1) (for

20 example Atlantis®, Archipel®), iodosulfuron and its salts and esters such as iodosulfuron-methyl and iodosulfuron-methyl-sodium (C2) (for example Hussar®, Hussar® OF, Sekkator®, Chekker®), foramsulfuron and its salts such as foramsulfuron-sodium (C3) (for example MaisTer®, Option®, Option® S), amidosulfuron and its salts such as amidosulfuron-sodium (C4) (for example

25 Gratil®), one or more sugarbeet herbicides from the group consisting of phenmedipham, desmedipham, ethofumesate, metamitron (C5) (for example Betanal® Quattro, Betanal® Crop, Betanal® Expert), isoproturon (C6), diflufenican (C7), ioxynil and its esters such as ioxynil octanoate (C8), bromoxynil and its esters such as bromoxynil octanoate (C9) (for example Quartz®, Tolkan®flo, First®,

30 Azur®), fenoxaprop-p-ethyl (C10), diclofop-methyl (C11), ethoxysulfuron and its salts such as ethoxysulfuron-sodium (C12). In this context, the terms C1-C12 encompass all of the herbicides listed before the term in question, preferably the herbicides

which have been mentioned explicitly. For example, the term C1 encompasses mesosulfuron and all of its salts and esters, preferably mesosulfuron-methyl and mesosulfuron-methyl-sodium, and the term C5 encompasses phenmedipham, desmedipham, ethofumesate and metamitron and their combinations.

5

In addition to the adjuvants according to the invention and one or more agrochemical active substances, the agrochemical compositions according to the invention may also comprise further components, for example formulation auxiliaries such as anti-drift agents, substances for influencing moisture (humectants), fertilizers such as

10 ammonium sulfate, urea or compound fertilizers, for example phosphorus-, potash- and nitrogen-based compound fertilizers, such as P,K,N fertilizers, or commercially available surfactants other than those of the formula (I), such as nonionic, cationic, anionic, betainic or polymeric surfactants, stabilizers such as pH stabilizers, biocides, UV stabilizers, antifoams, synthetic or natural polymers, solvents, for example polar  
15 solvents such as waters or alcohols, or unpolar solvents such as saturated or unsaturated aliphatic solvents, which may be branched or unbranched, or aromatic solvents, such as Solvesso® 100, Solvesso® 150 or Solvesso® 200 or xylene.

These agrochemical compositions and their use are likewise novel and subject matter of the present invention.

20

The agrochemical compositions according to the invention have an outstanding agrochemical activity against harmful organisms such as harmful plants. The improved control of the harmful plants by the agrochemical compositions according to the invention makes it possible to reduce the application rate and/or to increase  
25 the safety margin. Both make sense both from the economical and the ecological angle.

In a preferred embodiment, agrochemical compositions according to the invention are characterized by a synergistically active content of a combination of the  
30 surfactants a) with fatty acid esters b) such as vegetable oils and agrochemical active substances c). In this context, it must be emphasized in particular that, as a rule, the agrochemical compositions of the invention have an inherent synergistic

action, even in combinations with application rates or weight ratios of a) : b): c) where synergism cannot be detected readily in each individual case, for example because the individual compounds are usually employed in very different application rates in the combination or else because even the individual compounds alone effect  
5 very good control of the harmful plants.

The agrochemical compositions according to the invention can be prepared by customary processes, for example mixing by grinding, dissolving or dispersing the individual components, preferably at room temperature. If other auxiliaries are  
10 present, they are preferably likewise incorporated at room temperature. In general, the sequence in which the individual components are added is of no decisive importance.

The components a), b) and c) of the herbicidal compositions according to the  
15 invention may be present together in a readymix which can then be applied in the customary fashion, for example in the form of a spray mixture, or they can be formulated separately and applied for example together by the tank mix method or separately, for example in succession. When the components are formulated  
20 separately, components a), b) and c) can be formulated for example in each case individually, or else components a) and b), a) and c) or b) and c) can be formulated jointly and the third component in each case is formulated separately.

The adjuvants and agrochemical compositions according to the invention and their components can be formulated in various ways, depending on the prevailing  
25 biological and/or chemical-physical parameters. The following are examples of suitable formulation possibilities: water-soluble concentrates, microemulsions (ME), emulsifiable concentrates (EC), emulsions (EW) such as oil-in-water and water-in-oil emulsions, sprayable solutions, suspension concentrates (SC), suspoemulsion  
30 concentrates (SE), oil- or water-based dispersions, oil-miscible solutions, capsule suspensions (CS) and ULV formulations. If the agrochemical active substances c) are formulated separately, they may also be present as a solid formulation, for example as a dust (DP), seed-dressing material, granules for spreading and soil

application, granulates (GR) in the form of microgranules, spray granules, coated granules and adsorption granules, water-dispersible granules (WG), water-soluble granules (SG), microcapsules, waxes, wettable powders (WP) and water-soluble powders (SP).

5

The preparation processes and formulation types are known in principle and are described, for example, in: Winnacker-Küchler, "Chemische Technologie" [Chemical Technology], Volume 7, C. Hauser Verlag Munich, 4<sup>th</sup> Ed. 1986, Wade van Valkenburg, "Pesticide Formulations", Marcel Dekker, N.Y., 1973; K. Martens, "Spray Drying" Handbook, 3rd Ed. 1979, G. Goodwin Ltd. London; H. Mollet, A. Grubenmann, "Formulierungstechnik" [Formulation Technology], Wiley-VCH, Weinheim 2000.

10

The formulation auxiliaries required, such as inert materials, surfactants, solvents and additives, are also known and are described, for example, in Watkins, "Handbook of Insecticide Dust Diluents and Carriers", 2nd Ed., Darland Books, Caldwell N.J., H.v. Olphen, "Introduction to Clay Colloid Chemistry"; 2nd Ed., J. Wiley & Sons, N.Y.; C. Marsden, "Solvents Guide"; 2nd Ed., Interscience, N.Y. 1963; McCutcheon's "Detergents and Emulsifiers Annual", MC Publ. Corp., Ridgewood N.J.; Sisley and Wood, "Encyclopedia of Surface Active Agents", Chem. Publ. Co. Inc., N.Y. 1964; Schönfeldt, "Grenzflächenaktive Äthylenoxidaddukte" [Surface-active ethylene oxide adducts], Wiss. Verlagsgesell., Stuttgart 1976; Winnacker-Küchler, "Chemische Technologie", Volume 7, C. Hauser Verlag Munich, 4<sup>th</sup> Ed. 1986.

20

Based on these formulations, it is also possible to prepare combinations with other agrochemical active substances such as herbicides, fungicides, insecticides, safeners, fertilizers and/or growth regulators, for example in the form of a readymix or a tank mix.

25

Wettable (sprayable) powders are products which are uniformly dispersible in water and which, besides the components a), b) and/or c), optionally comprise diluents or

30

inert materials and further ionic and/or nonionic surfactants (wetters, dispersants), for example polyoxyethylated alkylphenols, polyoxyethylated fatty alcohols, polyoxyethylated fatty amines, fatty alcohol polyglycol ether sulfates,

alkanesulfonates, alkylbenzenesulfonates, sodium lignosulfonate, sodium 2,2'-

- 5 dinaphthylmethane-6,6'-disulfonate, sodium dibutylnaphthalenesulfonate or else sodium oleoylmethyltauride. To prepare the wettable powders, the component a) and/or b) and/or c) are ground finely, for example in customary apparatuses such as hammer mills, blower mills and air-jet mills, and mixed with the formulation auxiliaries, either simultaneously or subsequently.

10

Emulsifiable concentrates are prepared by dissolving the surfactant a) and/or fatty acid ester b) such as vegetable oil and/or agrochemical active substance c) in an organic solvent, for example butanol, cyclohexanone, dimethylformamide, xylene or else higher-boiling aromatics or hydrocarbons or mixtures of the organic solvents

15 with addition of one or more ionic and/or nonionic surfactants (emulsifiers).

Examples of emulsifiers which may be used are: calcium salts of alkylarylsulfonic acid, such as calcium dodecylbenzenesulfonate, or nonionic emulsifiers such as fatty acid polyglycol esters, alkylaryl polyglycol ethers, fatty alcohol polyglycol ethers, propylene oxide/ethylene oxide condensates, alkyl polyethers, sorbitan esters such 20 as, for example, sorbitan fatty acid esters, or polyoxyethylene sorbitan esters such as, for example, polyoxyethylene sorbitan fatty acid esters.

Dusts are obtained by grinding the surfactant a) and/or vegetable oil b) and/or agrochemical active substance c) with finely divided solid materials, for example 25 talc, natural clays such as kaolin, bentonite and pyrophyllite, or diatomaceous earth.

Suspension concentrates can be water- or oil-based. They can be prepared, for example by wet grinding by means of commercially available bead mills and, if appropriate, addition of further surfactants as have already been mentioned for

30 example above in the case of the other formulation types.

Emulsions, for example oil-in-water emulsions (EW), can be prepared for example by means of stirrers, colloid mills and/or static mixers using aqueous organic solvents and, if appropriate, further surfactants as have already been mentioned for example above in the case of the other formulation types.

5

Granules can be prepared either by spraying the surfactant a) and/or fatty acid ester b) such as vegetable oil and/or agrochemical active substance c) onto adsorptive, granulated inert material or by applying active ingredient concentrates to the surface of carriers such as sand, kaolinates or granulated inert material with the aid of

10 adhesives, for example polyvinyl alcohol, sodium polyacrylate or else mineral oils.

Suitable surfactants a) and/or fatty acid esters b) such as vegetable oil and/or agrochemical active substances c) may also be granulated in the manner conventionally used for the production of fertilizer granules, if desired in a mixture with fertilizers.

15 As a rule, water-dispersible granules are prepared by conventional processes such as spray drying, fluidized-bed granulation, disk granulation, mixing with high-speed mixers and extrusion without solid inert material. Regarding the production of disk granules, fluidized-bed granules, extruder granules and spray granules, see, for example, the methods in "Spray-Drying Handbook" 3rd Ed. 1979, G. Goodwin Ltd.,

20 London; J.E. Browning, "Agglomeration", Chemical and Engineering 1967, page 147 et seq.; "Perry's Chemical Engineer's Handbook", 5th Ed., McGraw-Hill, New York 1973, pp. 8-57.

For further details on the formulation of crop protection products, see, for example,

25 G.C. Klingman, "Weed Control as a Science", John Wiley and Sons, Inc., New York, 1961, pages 81-96 and J.D. Freyer, S.A. Evans, "Weed Control Handbook", 5th Ed., Blackwell Scientific Publications, Oxford, 1968, pages 101-103.

In addition, the abovementioned active substance formulations may comprise, if appropriate, additives such as adhesives, wetters, dispersants, emulsifiers, penetrants, preservatives, antifreeze agents, solvents, fillers, carriers, colorants,

antifoams, evaporation inhibitors, pH regulators or viscosity regulators which are customary in each case.

For use, the formulations, which are present in commercially available form, are, if

- 5 appropriate, diluted in the customary manner, for example using water in the case of wettable powders and water-dispersible granules. Preparations in the form of dusts and granules for soil or broadcasting application are conventionally not diluted any further with other inert substances prior to use.
- 10 The agrochemical compositions according to the invention can be employed for example by application to the harmful organisms or the locations at which they occur, for example by spraying. The agrochemical active substances c) to be used in accordance with the invention are generally applied together with the surfactants a) and fatty acid esters b), such as vegetable oils, or in succession, preferably in the
- 15 form of a spray mixture comprising the surfactants a), the fatty acid esters b), such as vegetable oils, and the agrochemical active substances c) in effective amounts and, if appropriate, further customary auxiliaires. Preparation of the spray mixture is preferably based on water and / or an oil, for example a vegetable oil, or a high-boiling hydrocarbon such as kerosene or paraffin. The agrochemical compositions
- 20 according to the invention can be realized for example as a tank mix or via a coformulation.

As a rule, the agrochemical formulations comprise from 0.1 to 99 percent by weight, in particular 2 to 95% by weight, of agrochemical active substances, the following

- 25 concentrations being generally customary, depending on the formulation type: in wettable powders, the active substance concentration generally amounts to approximately 10 to 90% by weight, the remainder to 100% by weight being composed of customary formulation constituents. In the case of emulsifiable concentrates, the active substance concentration can amount to approximately 1 to
- 30 90% by weight, preferably 5 to 80% by weight. Formulations in the form of dusts comprise 1 to 30% by weight of active substance, preferably in most cases 5 to 20% by weight of active substance, while sprayable solutions comprise approximately

0.05 to 80, preferably 2 to 50, % by weight of active substance. In the case of water-dispersible granules, the active substance content depends partly on whether the active compound is present in liquid or solid form and on the granulation aids, fillers and the like which are being used. In the case of the water-dispersible granules, the  
5 active substance content is, for example, between 1 and 95% by weight, preferably between 10 and 80% by weight. The percentages stated above may also be lower or higher in individual cases.

On application, the weight ratio agrochemical active substance c) : adjuvant  
10 according to the invention is generally in the range of from 1 : 10,000 to 100 : 1, preferably 1 : 1000 to 10 : 1, especially preferably 1 : 100 to 1 : 1, depending on the efficacy of the agrochemical active substance in question.

On application, the concentration of agrochemical active substance c) is generally  
15  $10^{-6}$  to 10% by weight, preferably  $10^{-5}$  to 4% by weight, especially preferably  $10^{-4}$  to 0.1% by weight, in the composition applied, for example the spray mixture, at an application rate of from 1 to 5000 l/ha, preferably 50 to 1000 l/ha. The concentration of adjuvant according to the invention is generally 0.001 to 10% by weight, preferably 0.005 to 5% by weight, especially preferably 0.05 to 3% by weight, in the  
20 composition applied, for example the spray mixture, at an application rate of from 1 to 5,000 l/ha, preferably 50 to 1,000 l/ha.

In addition to the components a), b) and c), the agrochemical compositions according to the invention preferably additionally comprise water and, if appropriate,  
25 organic solvents and, preferably, they are formulated in the form of an aqueous concentrated dispersion or emulsion or prepared as a tank mix in the form of a dilute dispersion, emulsion or solution with a dilution level down to that of the ready-to-use spray mixture. Especially preferred is an agrochemical composition which is prepared as a tank mix, comprising, for use, the preferred amounts of surfactant a),  
30 fatty acid ester b), such as vegetable oil, and agrochemical active substance c).

- For use, concentrated formulations which are present in commercially available form are, if appropriate, diluted in the customary fashion, for example by means of water in the case of wettable powders, emulsifiable concentrates, dispersions and water-dispersible granules. Preparations in the form of dusts, spray granules, absorption  
5 granules, sprayable solutions and spray mixtures prepared as tank mixes are not conventionally diluted further with additional inert substances prior to use. It may be advantageous or necessary to add further amounts of surfactants a), fatty acid esters b), such as vegetable oil and/or other conventional auxiliaries, in particular self-emulsifying oils or liquid paraffins, to the spray mixtures.
- 10 The application rate required of the agrochemical active substances c) varies with the external conditions such as temperature, humidity and the nature of the herbicide used. It can vary within wide limits, for example between 0.001 and 10 kg/ha or more of active substance, but it is preferably between 0.005 and 5 kg/ha.
- 15 The agrochemical compositions according to the invention are preferably herbicidal compositions which have an outstanding herbicidal activity against a broad spectrum of economically important monocotyledonous and dicotyledonous harmful plants. The active ingredients also act efficiently on perennial weeds which produce shoots  
20 from rhizomes, rootstocks or other perennial organs and which are difficult to control. In this context, it does not matter whether the substances are applied before sowing, pre-emergence or post-emergence. Specific examples may be mentioned of some representatives of the monocotyledonous and dicotyledonous weed flora which can be controlled by the herbicidal compositions according to the invention, without the  
25 enumeration being a restriction to certain species.

Examples of weed species on which the herbicidal compositions act efficiently are, from amongst the monocotyledonous weed species, *Apera spica venti*, *Avena spp.*, *Alopecurus spp.*, *Brachiaria spp.*, *Digitaria spp.*, *Lolium spp.*, *Echinochloa spp.*,  
30 *Panicum spp.*, *Phalaris spp.*, *Poa spp.*, *Setaria spp.* and *Bromus spp.* such as *Bromus catharticus*, *Bromus secalinus*, *Bromus erectus*, *Bromus tectorum* and *Bromus japonicus*, and *Cyperus* species from the annual group, and, among the

perennial species, Agropyron, Cynodon, Imperata and Sorghum and also perennial Cyperus species.

In the case of the dicotyledonous weed species, the spectrum of action extends to

- 5 genera such as, for example, Abutilon spp., Amaranthus spp., Chenopodium spp., Chrysanthemum spp., Galium spp. such as Galium aparine, Ipomoea spp., Kochia spp., Lamium spp., Matricaria spp., Pharbitis spp., Polygonum spp., Sida spp., Sinapis spp., Solanum spp., Stellaria spp., Veronica spp. and Viola spp., Xanthium spp., among the annuals, and Convolvulus, Cirsium, Rumex and Artemisia in the  
10 case of the perennial weeds.

The active ingredients according to the invention also act outstandingly efficiently on harmful plants which are found under the specific cultures in rice, such as, for example, Echinochloa, Sagittaria, Alisma, Eleocharis, Scirpus and Cyperus.

- 15 If the herbicidal compositions according to the invention are applied to the soil surface before germination, the weed seedlings are either prevented completely from emerging or else the weeds grow until they have reached the cotyledon stage, but then their growth stops, and, eventually, after three to four weeks have elapsed, they  
20 die completely.

- If the herbicidal compositions according to the invention are applied post-emergence to the green parts of the plants, growth likewise stops drastically a very short time after the treatment, and the weed plants remain at the growth stage of the point of  
25 time of application, or they die completely after a certain time, so that in this manner competition by the weeds, which is harmful to the crop plants, is eliminated very early and in a sustained manner.

- The herbicidal compositions according to the invention are distinguished by a rapidly  
30 commencing and long-lasting herbicidal action. As a rule, the rainfastness of the active substances in the combinations according to the invention is advantageous. A particular advantage is that the dosages used in the herbicidal compositions and the

effective dosages of herbicidal compounds can be adjusted to such low a level that their soil action is optimally low. This does not only allow them to be employed in sensitive crops in the first place, but groundwater contaminations are virtually avoided. The active ingredient combination according to the invention allows the 5 required application rate of the active substances to be reduced considerably.

When adjuvants according to the invention and agrochemical active substances, in particular herbicides, are used jointly, superadditive (= synergistic) effects are observed in the preferred embodiment. This means that the effect in the 10 combinations exceeds the expected total of the effects of the individual components employed. The synergistic effects allow the application rate to be reduced, a broader spectrum of broad-leaved weeds and grass weeds to be controlled, the herbicidal effect to commence more rapidly, the duration of action to be longer, the harmful plants to be controlled better while using only one, or few, applications, and the 15 application window to be extended. In some cases, use of the compositions also reduces the amount of harmful constituents, such as nitrogen or oleic acid, and their entry into the ground.

The abovementioned properties and advantages are necessary for weed control 20 practice to keep agricultural crops free from undesired competing plants, and thus to ensure and/or increase yield levels from the qualitative and quantitative angle. These novel compositions markedly exceed the technical state of the art with a view to the properties described.

25 While the herbicidal compositions according to the invention have an outstanding herbicidal activity against monocotyledonous and dicotyledonous weeds, crop plants of economically important crops, for example dicotyledonous crops such as soya, cotton, oilseed rape, sugarbeet, or graminaceous crops such as wheat, barley, rye, oats, sorghum and millet, rice or maize, are damaged only to a minor extent, if at all. 30 This is why the present compounds are highly suitable for the selective control of undesired plant growth in plantations of agricultural crops or of ornamentals.

In addition, the herbicidal compositions according to the invention have outstanding growth-regulatory properties in crop plants. They engage in the plants' metabolism in a regulatory manner and can thus be employed for provoking direct effects on plant constituents and to facilitate harvesting such as, for example, by triggering

- 5 desiccation and stunted growth. Moreover, they are also suitable for the general control and inhibition of undesired vegetative growth without simultaneously destroying the plants. Inhibition of vegetative growth is very important in a large number of monocotyledonous and dicotyledonous crops since lodging can thus be reduced, or prevented completely.

10

Owing to their herbicidal and plant-growth-regulatory properties, the herbicidal compositions according to the invention can also be employed for controlling harmful plants in crops of genetically modified plants which are known or yet to be developed. As a rule, the recombinant plants are distinguished by specific

- 15 advantageous characteristics, for example by resistances to certain pesticides, in particular certain herbicides, resistances to plant diseases or the causative organisms of plant diseases such as specific insects or microorganisms such as fungi, bacteria or viruses. Other specific characteristics relate, for example, to the harvested material with regard to quantity, quality, storability, composition and  
20 specific constituents. Thus, for example, transgenic plants are known whose starch content is increased, or whose starch quality is altered, or those where the harvested material has a different fatty acid composition.

- The use of the compositions according to the invention in economically important  
25 transgenic crops of useful plants and ornamentals, for example of graminaceous crops such as wheat, barley, rye, oats, sorghum and millet, rice and maize, or else crops of sugarbeet, cotton, soya, oilseed rape, potatoes, tomatoes, peas and other vegetables, is preferred. Preferably, the compositions according to the invention can be employed as herbicides in crops of useful plants which resist the phytotoxic  
30 effects of the herbicides, or have been made to resist these effects by recombinant techniques.

When using the herbicidal compositions according to the invention in transgenic crops, effects are frequently observed in addition to the effects against harmful plants to be observed in other crops, which are specific for the application in the transgenic crop in question, for example a modified or specifically widened weed

- 5 spectrum which can be controlled, modified application rates which may be employed for application, preferably good combining ability with the herbicides to which the transgenic crop is resistant, and an effect on growth and yield level of the transgenic crop plants.
- 10 The present invention therefore furthermore also relates to a method for controlling undesired vegetation, preferably in crops of plants such as cereals (for example wheat, barley, rye, oats, rice, maize, sorghum and millet), sugar beet, sugar cane, oilseed rape, cotton and soya, especially preferred in monocotyledonous plants such as cereals, for example wheat, barley, rye, oats, and their hybrids such as triticale,
- 15 rice, maize, sorghum and millet, where one or more herbicidal compositions according to the invention are applied to the harmful plants, plant parts, seeds of the plants or the area on which the plants grow, for example the area under cultivation.

The plant crops may also be genetically modified or have been obtained by mutation  
20 selection; they preferably tolerate acetolactate synthase (ALS) inhibitors.

The invention therefore also relates to the use of the herbicidal compositions according to the invention for controlling harmful plants, preferably in plant crops.

25 The herbicidal compositions according to the invention can also be employed nonselectively for controlling undesired vegetation, for example in plantation crops, on verges, squares, industrial terrain or rail tracks.

30 The agrochemical compositions according to the invention, in particular herbicidal compositions, can exist not only as mixed formulations, if appropriate together with other agrochemical active substances, auxiliaires such as additives and/or formulation aids, which are then diluted with water and applied as usual, but also as

what are known as tank mixes by jointly diluting, with water, the components which have been formulated separately or partially separately.

Owing to the relatively low application rate of the herbicidal compositions according

5 to the invention, they are generally very well tolerated. In particular, a reduction in the absolute application rate can be achieved by the combinations according to the invention, compared with the individual use of a herbicidal active substance.

The invention therefore also relates to a method of controlling harmful plants, preferably for the selective control of harmful plants in plant crops, which comprises

10 applying, for example pre-emergence, post-emergence or pre- and post-emergence, preferably pre-emergence, a herbicidally active amount of the abovementioned herbicides c) in combination with at least one of the surfactants a) and at least one fatty acid ester b), such as vegetable oil, to the plants, plant parts, seeds of the plants or the area on which the plants grow, for example the area under cultivation,

15 either jointly or in succession.

In a preferred method variant, the herbicides c) are applied at application rates of from 0.005 (preferably 0.1) to 5,000 g of active substance/ha, especially preferably 0.5 to 1,000 g of active substance/ha. It is furthermore especially preferred to apply

20 the active substances in the form of a coformulation or in the form of tank mixes, where the individual components, for example in the form of formulations, are jointly mixed in the tank with water and the resulting spray mixture is applied.

Since the crop plant compatibility of the combinations according to the invention is

25 extremely good, combined with a very high degree of control of the harmful plants, the combinations according to the invention can be considered as selective. In a preferred embodiment, herbicidal compositions with the active substance combinations according to the invention are therefore employed for selectively controlling undesired plants.

30

If, if desired, the compatibility and/or selectivity of the herbicidal compositions according to the invention is to be increased even further, it may be advantageous to

apply them together with safeners or antidotes, either jointly in a mixture or staggered in time.

Compounds which are suitable as safeners or antidotes for the herbicidal

- 5 compositions according to the invention are known, for example, from EP-A-333 131 (ZA-89/1960), EP-A-269 806 (US-A-4,891,057), EP-A-346 620 (AU-A-89/34951) and the international patent applications PCT/EP 90/01966 (WO-91108202) and PCT/EP 90/02020 (WO-911078474) and literature cited therein or can be prepared by the processes described therein. Further suitable safeners are known from EP-A-94 349  
10 (US-A-4,902,304), EP-A-191 736 (US-A-4,881,966) and EP-A-0  
492 366 and the literature cited therein.

In a preferred embodiment, the herbicidal compositions of the present invention therefore contain an additional content of one or more compounds which act as  
15 safeners or antidotes.

Especially preferred antidotes or safeners or groups of compounds which are suitable as safeners or antidotes for the above-described herbicidal compositions of the invention are, inter alia:

- 20 a) compounds of the dichlorophenylpyrazoline-3-carboxylic acid type, preferably compounds such as ethyl 1-(2,4-dichlorophenyl)-5-(ethoxycarbonyl)-5-methyl-2-pyrazoline-3-carboxylate (compound S1 –1, mefenpyr-diethyl) and related compounds as are described in the international application WO 91/07874  
25 (PCT/EP 90102020);  
b) dichlorophenylpyrazolecarboxylic acid derivatives, preferably compounds such as ethyl 1-(2,4-dichlorophenyl)-5-methylpyrazole-3-carboxylate (compound S1-2), ethyl 1-(2,4-dichlorophenyl)-5-isopropylpyrazole-3-carboxylate (compound S1-3),  
30 ethyl 1-(2,4-dichlorophenyl)-5-(1,1-dimethylethyl)pyrazole-3-carboxylate (compound S1-4),

ethyl 1-(2,4-dichlorophenyl)-5-phenylpyrazole-3-carboxylate (compound S1-5) and related compounds as are described in EP-A-0 333 131 and EP-A-0 269 806;

- c) compounds of the triazolecarboxylic acids type, preferably compounds such as ethyl 1-(2,4-dichlorophenyl)-5-trichloromethyl-(1H)-1,2,4-triazole-3-carboxylate (compound S1-6, fenchlorazole) and related compounds (see EP-A-0 174 562 and EP-A-0 346 620);
- d) compounds of the dichlorobenzyl-2-isoxazoline-3-carboxylic acid type, compounds of the 5-benzyl- or 5-phenyl-2-isoxazoline-3-carboxylic acid type, preferably compounds such as ethyl 5-(2,4-dichlorobenzyl)-2-isoxazoline-3-carboxylate (compound S1 -7) or ethyl 5-phenyl-2-isoxazoline-3-carboxylate (compound S1-8), and related compounds as are described in international patent application WO 91/08202 (PCT/EP 90/01966);
- e) compounds of the 8-quinolinoxyacetic acid type, preferably compounds such as 1-methylhex-1-yl (5-chloro-8-quinolinoxy)acetate (S2-1; cloquintocet-mexyl),  
1,3-dimethylbut-1-yl (5-chloro-8-quinolinoxy)acetate (S2-2),  
4-allyloxybutyl (5-chloro-8-quinolinoxy)acetate (S2-3),  
1-allyloxyprop-2-yl (5-chloro-8-quinolinoxy)acetate (S2-4),  
ethyl (5-chloro-8-quinolinoxy)acetate (S2-5),  
methyl (5-chloro-8-quinolinoxy)acetate (S2-6),  
allyl (5-chloro-8-quinolinoxy)acetate (S2-7),  
2-(2-propylideneiminoxy)-1-ethyl (5-chloro-8-quinolinoxy)acetate (S2-8),  
2-oxoprop-1-yl (5-chloro-8-quinolinoxy)acetate (S2-9) and related compounds as are described in EP-A-0 086 750, EP-A-0 094 349 and EP-A-0 191 736 or EP-A-0 492 366;
- f) compounds of the (5-chloro-8-quinolinoxy)malonic acid type, preferably compounds such as diethyl (5-chloro-8-quinolinoxy)malonate, diallyl (5-chloro-8-quinolinoxy)malonate, methyl ethyl (5-chloro-8-quinolinoxy)malonate and related compounds as have been described and proposed in German patent application EP-A-0 582 198;

- g) active substances of the type of the phenoxyacetic acid derivatives or phenoxypropionic acid derivatives or of the aromatic carboxylic acids such as, for example, 2,4-dichlorophenoxyacetic acid (and esters) (2,4-D), 4-chloro-2-methylphenoxypropionic acid (mecoprop), MCPA or 3,6-dichloro-  
5 2-methoxybenzoic acid (and esters) (dicamba).
- h) compounds of the 5,5-diphenyl-2-isoxazoline-3-carboxylic acid type, preferably ethyl 5,5-diphenyl-2-isoxazoline-3-carboxylate (S3-1, isoxadifen-ethyl).
- i) compounds which are known as safeners, for example for rice, such as  
10 fenclorim (= 4,6-dichloro-2-phenylpyrimidine, Pesticide Manual, 11<sup>th</sup> Edition, 1997, pp. 511-512), dimepiperate (= S-1-methyl-1-phenylethyl piperidine-1-thiocarboxylate, Pesticide Manual, 11<sup>th</sup> Edition, 1997, pp. 404-405), daimuron (= 1-(1 -methyl-1-phenylethyl)-3-p-tolylurea, Pesticide Manual, 11<sup>th</sup> Edition, 1997, p. 330), cumyluron (= 3-(2-chlorophenylmethyl)-1-(1 -methyl-  
15 1-phenylethyl)urea, JP-A-60/087254), methoxyphenone (= 3,3'-dimethyl-4-methoxybenzophenone, CSB (= 1-bromo-4-(chloromethylsulfonyl)benzene, CAS-Reg. No. 54091-06-4)).

In addition, at least some of the abovementioned compounds are described in  
20 EP-A-0 640 587, which is herewith referred to for disclosure purposes.

- j) A further important group of compounds which are suitable as safeners and antidotes is known from WO 95/07897.
- 25 The safeners (antidotes) of the above groups a) to j) reduce or prevent phytotoxic effects which may be observed when the herbicidal compositions according to the invention are employed in crops of useful plants, without adversely affecting the efficacy of the herbicides against harmful plants. This makes it possible considerably to widen the spectrum of application of the herbicidal compositions according to the  
30 invention; in particular, the use of safeners makes possible the application of herbicidal compositions which could previously only be employed to a limited extent

or with insufficient success, i.e. of combinations which, at low dosages with a poor spectrum of action, led to insufficient control of the harmful plants without safeners.

- Components a), b) and c) of the herbicidal compositions according to the invention  
5 and the abovementioned safeners can be applied jointly (for example as readymix or by the tank mix method) or in succession in any desired sequence. The weight ratio safener:herbicide (compound(s) of the formula (I) and/or their salts) can vary within wide limits and is preferably in the range of from 1 : 100 to 100 : 1, in particular of from 1 : 100 to 50 : 1. The amounts of herbicide(s) and safener(s) which are optimal  
10 in each case usually depend on the type of the herbicidal composition and/or on the safener used, and also on the nature of the plant stand to be treated.

Depending on their properties, the safeners can be used for pretreating the seed of the crop plant (seed dressing) or introduced into the seed furrows prior to sowing or  
15 applied together with the herbicide mixture before or after emergence of the plants. Pre-emergence treatment includes both the treatment of the area under cultivation before sowing and the treatment of the areas under cultivation where seed has been sown, but growth is as yet not present. The joint application with the herbicide mixture is preferred. Tank mixes or readymixes can be employed for this purpose.  
20

The application rates required, of the safeners, can vary within wide limits, depending on the indication and the herbicide used; they are, as a rule, in the range of from 0.001 to 5 kg, preferably 0.005 to 0.2 kg, of active substance per hectare.

25 The herbicidal compositions according to the invention can be applied in the customary fashion, for example with water as carrier in spray mixture quantities of approximately 5 to 4000 liters/ha. Application of the compositions by what is known as the low-volume and ultra-low-volume methods (ULV) is also possible, as is their application in the form of granules and microgranules.

30 A preferred use relates to application of herbicidal compositions which contain components a), b) and c) in a synergistically active amount.

The invention also extends to mixtures of one or more surfactants a) with one or more fatty acid esters b), such as vegetable oils, and one or more herbicides c). In addition, one, two or more agrochemical active substances other than the herbicides c) (for example insecticides, fungicides, safeners) may be present in the herbicidal 5 compositions of the invention for complementing their properties, usually in minor amounts.

Preferred examples of the herbicidal compositions according to the invention are combinations of surfactants of the Sapogenat®T series (for example

10 Sapogenat®T020, Sapogenat®T040, Sapogenat®T060, Sapogenat®T080, Sapogenat®T100 or Sapogenat®T110) with vegetable oils, for example rapeseed oils such as rapeseed oil methyl ester, and herbicidal active substances c), such as the herbicides C1-C12, in particular the following combinations of surfactants of the 15 Sapogenat®T series (hereinbelow referred to as Sapogenat) with rapeseed oils such as rapeseed oil methyl ester and the herbicides C1 – C12, without this being intended as a limitation to the combinations which are mentioned explicitly:

Sapogenat + Actirob B + C1, Sapogenat + Hasten + C1, Sapogenat + Mero + C1,  
Sapogenat + Rako-Binol + C1, Sapogenat + Phytorob B + C1, Sapogenat + Edenor  
20 + C1, Sapogenat + Agnique + C1;  
Sapogenat + Actirob B + C2, Sapogenat + Hasten + C2, Sapogenat + Mero + C2,  
Sapogenat + Rako-Binol + C2, Sapogenat + Phytorob B + C2, Sapogenat + Edenor  
+ C2, Sapogenat + Agnique + C2;  
Sapogenat + Actirob B + C3, Sapogenat + Hasten + C3, Sapogenat + Mero + C3,  
25 Sapogenat + Rako-Binol + C3, Sapogenat + Phytorob B + C3, Sapogenat + Edenor  
+ C3, Sapogenat + Agnique + C3;  
Sapogenat + Actirob B + C4, Sapogenat + Hasten + C4, Sapogenat + Mero + C4,  
Sapogenat + Rako-Binol + C4, Sapogenat + Phytorob B + C4, Sapogenat + Edenor  
+ C4, Sapogenat + Agnique + C4;  
30 Sapogenat + Actirob B + C5, Sapogenat + Hasten + C5, Sapogenat + Mero + C5,  
Sapogenat + Rako-Binol + C5, Sapogenat + Phytorob B + C5, Sapogenat + Edenor  
+ C5, Sapogenat + Agnique + C5;

- Sapogenat + Actirob B + C6, Sapogenat + Hasten + C6, Sapogenat + Mero + C6,  
 Sapogenat + Rako-Binol + C6, Sapogenat + Phytorob B + C6, Sapogenat + Edenor  
 + C6, Sapogenat + Agnique + C6;
- Sapogenat + Actirob B + C7, Sapogenat + Hasten + C7, Sapogenat + Mero + C7,
- 5 Sapogenat + Rako-Binol + C7, Sapogenat + Phytorob B + C7, Sapogenat + Edenor  
 + C7, Sapogenat + Agnique + C7;
- Sapogenat + Actirob B + C8, Sapogenat + Hasten + C8, Sapogenat + Mero + C8,  
 Sapogenat + Rako-Binol + C8, Sapogenat + Phytorob B + C8, Sapogenat + Edenor  
 + C8, Sapogenat + Agnique + C8;
- 10 Sapogenat + Actirob B + C9, Sapogenat + Hasten + C9, Sapogenat + Mero + C9,  
 Sapogenat + Rako-Binol + C9, Sapogenat + Phytorob B + C9, Sapogenat + Edenor  
 + C9, Sapogenat + Agnique + C9;
- Sapogenat + Actirob B + C10, Sapogenat + Hasten + C10, Sapogenat + Mero +  
 C10, Sapogenat + Rako-Binol + C10, Sapogenat + Phytorob B + C10, Sapogenat +
- 15 Edenor + C10, Sapogenat + Agnique + C10;
- Sapogenat + Actirob B + C11, Sapogenat + Hasten + C11, Sapogenat + Mero +  
 C11, Sapogenat + Rako-Binol + C11, Sapogenat + Phytorob B + C11, Sapogenat +  
 Edenor + C11, Sapogenat + Agnique + C11;
- Sapogenat + Actirob B + C12, Sapogenat + Hasten + C12, Sapogenat + Mero +
- 20 C12, Sapogenat + Rako-Binol + C12, Sapogenat + Phytorob B + C12, Sapogenat +  
 Edenor + C12, Sapogenat + Agnique + C12.

The above-described mixtures can be employed expediently together with one or more safeners. Examples of preferred safeners are

- 25 ethyl 1-(2,4-dichlorophenyl)-5-(ethoxycarbonyl)-5-methyl-2-pyrazoline-3-carboxylate  
 (S1-1, Mefenpyr-diethyl), 1-methylhex-1-yl (5-chloro-8-quinolinoxy)acetate (S2-1,  
 cloquintocet-mexyl) and ethyl 5,5-diphenyl-2-isoxazoline-3-carboxylate (S3-1,  
 isoxadifen-ethyl).
- 30 In the combinations mentioned, the use of a safener may be advantageous since potential damage to the crop plant, which may arise as the result of sulfonylurea derivatives or other herbicidally active compounds, can thus be reduced.

Furthermore, the safeners S1-1, S2-1 and S3-1 can be replaced advantageously by one or more compounds from the following group of safeners, or employed together with one or more of the following compounds:

- 5     •     ethyl 1-(2,4-dichlorophenyl)-5-methylpyrazole-3-carboxylate (S1-2),  
•     ethyl 1-(2,4-dichlorophenyl)-5-isopropylpyrazole-3-carboxylate (S1-3),  
•     ethyl 1-(2,4-dichlorophenyl)-5-(1,1-dimethylethyl)pyrazole-3-carboxylate (S1-4),  
•     ethyl 1-(2,4-dichlorophenyl)-5-phenylpyrazole-3-carboxylate (S1-5),  
10    •     ethyl 1-(2,4-dichlorophenyl)-5-trichloromethyl-(1H)-1,2,4-triazole-3-carboxylate (S1-6, fenchlorazol)  
•     ethyl 5-(2,4-dichlorobenzyl)-2-isoxazoline-3-carboxylate (S1-7),  
•     ethyl 5-phenyl-2-isoxazoline-3-carboxylate (S1-8),  
•     1,3-dimethylbut-1-yl (5-chloro-8-quinolinoxy)acetate (S2-2),  
15    •     4-allyloxybutyl (5-chloro-8-quinolinoxy)acetate (S2-3),  
•     1-allyloxyprop-2-yl (5-chloro-8-quinolinoxy)acetate (S2-4),  
•     ethyl (5-chloro-8-quinolinoxy)acetate (S2-5),  
•     methyl (5-chloro-8-quinolinoxy)acetate (S2-6),  
•     allyl (5-chloro-8-quinolinoxy)acetate (S2-7),  
20    •     2-(2-propylideneiminoxy)-1-ethyl (5-chloro-8-quinolinoxy)acetate (S2-8),  
•     2-oxoprop-1-yl (5-chloro-8-quinolinoxy)acetate (S2-9),  
•     diethyl (5-chloro-8-quinolinoxy)malonate,  
•     diallyl (5-chloro-8-quinolinoxy)malonate,  
•     methylethyl (5-chloro-8-quinolinoxy)malonate  
25    •     2,4-dichlorophenoxyacetic acid (ester) (2,4-D),  
•     4-chloro-2-methylphenoxypropionic ester (mecoprop),  
•     MCPA,  
•     3,6-dichloro-2-methoxybenzoic acid (ester) (dicamba).  
  
30    Preferred mixtures are:

- Sapogenat + Actirob B + S1-1 + C1, Sapogenat + Hasten + S1-1 + C1, Sapogenat + Mero + S1-1 + C1, Sapogenat + Rako-Binol + S1-1 + C1, Sapogenat + Phytorob B + S1-1 + C1, Sapogenat + Edenor + S1-1 + C1, Sapogenat + Agnique + S1-1 + C1; Sapogenat + Actirob B + S1-1 + C2, Sapogenat + Hasten + S1-1 + C2, Sapogenat +
- 5 Mero + S1-1 + C2, Sapogenat + Rako-Binol + S1-1 + C2, Sapogenat + Phytorob B + S1-1 + C2, Sapogenat + Edenor + S1-1 + C2, Sapogenat + Agnique + S1-1 + C2; Sapogenat + Actirob B + S1-1 + C3, Sapogenat + Hasten + S1-1 + C3, Sapogenat + Mero + S1-1 + C3, Sapogenat + Rako-Binol + S1-1 + C3, Sapogenat + Phytorob B + S1-1 + C3, Sapogenat + Edenor + S1-1 + C3, Sapogenat + Agnique + S1-1 + C3;
- 10 Sapogenat + Actirob B + S1-1 + C4, Sapogenat + Hasten + S1-1 + C4, Sapogenat + Mero + S1-1 + C4, Sapogenat + Rako-Binol + S1-1 + C4, Sapogenat + Phytorob B + S1-1 + C4, Sapogenat + Edenor + S1-1 + C4, Sapogenat + Agnique + S1-1 + C4; Sapogenat + Actirob B + S1-1 + C5, Sapogenat + Hasten + S1-1 + C5, Sapogenat + Mero + S1-1 + C5, Sapogenat + Rako-Binol + S1-1 + C5, Sapogenat + Phytorob B +
- 15 S1-1 + C5, Sapogenat + Edenor + S1-1 + C5, Sapogenat + Agnique + S1-1 + C5; Sapogenat + Actirob B + S1-1 + C6, Sapogenat + Hasten + S1-1 + C6, Sapogenat + Mero + S1-1 + C6, Sapogenat + Rako-Binol + S1-1 + C6, Sapogenat + Phytorob B + S1-1 + C6, Sapogenat + Edenor + S1-1 + C6, Sapogenat + Agnique + S1-1 + C6; Sapogenat + Actirob B + S1-1 + C7, Sapogenat + Hasten + S1-1 + C7, Sapogenat +
- 20 Mero + S1-1 + C7, Sapogenat + Rako-Binol + S1-1 + C7. Sapogenat + Phytorob B + S1-1 + C7, Sapogenat + Edenor + S1-1 + C7, Sapogenat + Agnique + S1-1 + C7; Sapogenat + Actirob B + S1-1 + C8, Sapogenat + Hasten + S1-1 + C8, Sapogenat + Mero + S1-1 + C8, Sapogenat + Rako-Binol + S1-1 + C8, Sapogenat + Phytorob B + S1-1 + C8, Sapogenat + Edenor + S1-1 + C8, Sapogenat + Agnique + S1-1 + C8;
- 25 Sapogenat + Actirob B + S1-1 + C9, Sapogenat + Hasten + S1-1 + C9, Sapogenat + Mero + S1-1 + C9, Sapogenat + Rako-Binol + S1-1 + C9, Sapogenat + Phytorob B + S1-1 + C9, Sapogenat + Edenor + S1-1 + C9, Sapogenat + Agnique + S1-1 + C9; Sapogenat + Actirob B + S1-1 + C10, Sapogenat + Hasten + S1-1 + C10, Sapogenat + Mero + S1-1 + C7, Sapogenat + Rako-Binol + S1-1 + C10, Sapogenat + Phytorob
- 30 B + S1-1 + C10, Sapogenat + Edenor + S1-1 + C10, Sapogenat + Agnique + S1-1 + C10;

- Sapogenat + Actirob B + S1-1 + C11, Sapogenat + Hasten + S1-1 + C11, Sapogenat + Mero + S1-1 + C11, Sapogenat + Rako-Binol + S1-1 + C11, Sapogenat + Phytorob B + S1-1 + C11, Sapogenat + Edenor + S1-1 + C11, Sapogenat + Agnique + S1-1 + C11;
- 5 Sapogenat + Actirob B + S1-1 + C12, Sapogenat + Hasten + S1-1 + C12, Sapogenat + Mero + S1-1 + C12, Sapogenat + Rako-Binol + S1-1 + C12, Sapogenat + Phytorob B + S1-1 + C12, Sapogenat + Edenor + S1-1 + C12, Sapogenat + Agnique + S1-1 + C12;
- 10 Sapogenat + Actirob B + S2-1 + C1, Sapogenat + Hasten + S2-1 + C1, Sapogenat + Mero + S2-1 + C1, Sapogenat + Rako-Binol + S2-1 + C1, Sapogenat + Phytorob B + S2-1 + C1, Sapogenat + Edenor + S2-1 + C1, Sapogenat + Agnique + S2-1 + C1; Sapogenat + Actirob B + S2-1 + C2, Sapogenat + Hasten + S2-1 + C2, Sapogenat + Mero + S2-1 + C2, Sapogenat + Rako-Binol + S2-1 + C2, Sapogenat + Phytorob B +
- 15 S2-1 + C2, Sapogenat + Edenor + S2-1 + 2, Sapogenat + Agnique + S2-1 + C2; Sapogenat + Actirob B + S2-1 + C3, Sapogenat + Hasten + S2-1 + C3, Sapogenat + Mero + S2-1 + C3, Sapogenat + Rako-Binol + S2-1 + C3, Sapogenat + Phytorob B + S2-1 + C3, Sapogenat + Edenor + S2-1 + C3, Sapogenat + Agnique + S2-1 + C3; Sapogenat + Actirob B + S2-1 + C4, Sapogenat + Hasten + S2-1 + C4, Sapogenat +
- 20 Mero + S2-1 + C4, Sapogenat + Rako-Binol + S2-1 + C4, Sapogenat + Phytorob B + S2-1 + C4, Sapogenat + Edenor + S2-1 + C4, Sapogenat + Agnique + S2-1 + C4; Sapogenat + Actirob B + S2-1 + C5, Sapogenat + Hasten + S2-1 + C5, Sapogenat + Mero + S2-1 + C5, Sapogenat + Rako-Binol + S2-1 + C5, Sapogenat + Phytorob B + S2-1 + C5, Sapogenat + Edenor + S2-1 + C5, Sapogenat + Agnique + S2-1 + C5;
- 25 Sapogenat + Actirob B + S2-1 + C6, Sapogenat + Hasten + S2-1 + C6, Sapogenat + Mero + S2-1 + C6, Sapogenat + Rako-Binol + S2-1 + C6, Sapogenat + Phytorob B + S2-1 + C6, Sapogenat + Edenor + S2-1 + C6, Sapogenat + Agnique + S2-1 + C6; Sapogenat + Actirob B + S2-1 + C7, Sapogenat + Hasten + S2-1 + C7, Sapogenat + Mero + S2-1 + C7, Sapogenat + Rako-Binol + S2-1 + C7, Sapogenat + Phytorob B +
- 30 S2-1 + C7, Sapogenat + Edenor + S2-1 + C7, Sapogenat + Agnique + S2-1 + C7;

- Sapogenat + Actirob B + S2-1 + C8, Sapogenat + Hasten + S2-1 + C8, Sapogenat + Mero + S2-1 + C8, Sapogenat + Rako-Binol + S2-1 + C8, Sapogenat + Phytrob B + S2-1 + C8, Sapogenat + Edenor + S2-1 + C8, Sapogenat + Agnique + S2-1 + C8; Sapogenat + Actirob B + S2-1 + C9, Sapogenat + Hasten + S2-1 + C9, Sapogenat +
- 5 Mero + S2-1 + C9, Sapogenat + Rako-Binol + S2-1 + C9, Sapogenat + Phytrob B + S2-1 + C9, Sapogenat + Edenor + S2-1 + C9, Sapogenat + Agnique + S2-1 + C9; Sapogenat + Actirob B + S2-1 + C10, Sapogenat + Hasten + S2-1 + C10, Sapogenat + Mero + S2-1 + C10, Sapogenat + Rako-Binol + S2-1 + C10, Sapogenat + Phytrob B + S2-1 + C10, Sapogenat + Edenor + S2-1 + C10, Sapogenat + Agnique + S2-1 +
- 10 C10;
- Sapogenat + Actirob B + S2-1 + C11, Sapogenat + Hasten + S2-1 + C11, Sapogenat + Mero + S2-1 + C11, Sapogenat + Rako-Binol + S2-1 + C11, Sapogenat + Phytrob B + S2-1 + C11, Sapogenat + Edenor + S2-1 + C11, Sapogenat + Agnique + S2-1 + C11;
- 15 Sapogenat + Actirob B + S2-1 + C12, Sapogenat + Hasten + S2-1 + C12, Sapogenat + Mero + S2-1 + C12, Sapogenat + Rako-Binol + S2-1 + C12, Sapogenat + Phytrob B + S2-1 + C12, Sapogenat + Edenor + S2-1 + C12, Sapogenat + Agnique + S2-1 + C12;
- 20 Sapogenat + Actirob B + S3-1 + C1, Sapogenat + Hasten + S3-1 + C1, Sapogenat + Mero + S3-1 + C1, Sapogenat + Rako-Binol + S3-1 + C1, Sapogenat + Phytrob B + S3-1 + C1, Sapogenat + Edenor + S3-1 + C1, Sapogenat + Agnique + S3-1 + C1; Sapogenat + Actirob B + S3-1 + C2, Sapogenat + Hasten + S3-1 + C2, Sapogenat + Mero + S3-1 + C2, Sapogenat + Rako-Binol + S3-1 + C2, Sapogenat + Phytrob B +
- 25 S3-1 + C2, Sapogenat + Edenor + S3-1 + C2, Sapogenat + Agnique + S3-1 + C2; Sapogenat + Actirob B + S3-1 + C3, Sapogenat + Hasten + S3-1 + C3, Sapogenat + Mero + S3-1 + C3, Sapogenat + Rako-Binol + S3-1 + C3, Sapogenat + Phytrob B + S3-1 + C3, Sapogenat + Edenor + S3-1 + C3, Sapogenat + Agnique + S3-1 + C3; Sapogenat + Actirob B + S3-1 + C4, Sapogenat + Hasten + S3-1 + C4, Sapogenat +
- 30 Mero + S3-1 + C4, Sapogenat + Rako-Binol + S3-1 + C4, Sapogenat + Phytrob B + S3-1 + C4, Sapogenat + Edenor + S3-1 + C4, Sapogenat + Agnique + S3-1 + C4;

- Sapogenat + Actirob B + S3-1 + C5, Sapogenat + Hasten + S3-1 + C5, Sapogenat + Mero + S3-1 + C5, Sapogenat + Rako-Binol + S3-1 + C5, Sapogenat + Phytorob B + S3-1 + C5, Sapogenat + Edenor + S3-1 + C5, Sapogenat + Agnique + S3-1 + C5; Sapogenat + Actirob B + S3-1 + C6, Sapogenat + Hasten + S3-1 + C6, Sapogenat + Mero + S3-1 + C6, Sapogenat + Rako-Binol + S3-1 + C6, Sapogenat + Phytorob B + S3-1 + C6, Sapogenat + Edenor + S3-1 + C6, Sapogenat + Agnique + S3-1 + C6; Sapogenat + Actirob B + S3-1 + C7, Sapogenat + Hasten + S3-1 + C7, Sapogenat + Mero + S3-1 + C7, Sapogenat + Rako-Binol + S3-1 + C7, Sapogenat + Phytorob B + S3-1 + C7, Sapogenat + Edenor + S3-1 + C7, Sapogenat + Agnique + S3-1 + C7; Sapogenat + Actirob B + S3-1 + C8, Sapogenat + Hasten + S3-1 + C8, Sapogenat + Mero + S3-1 + C8, Sapogenat + Rako-Binol + S3-1 + C8, Sapogenat + Phytorob B + S3-1 + C8, Sapogenat + Edenor + S3-1 + C8, Sapogenat + Agnique + S3-1 + C8; Sapogenat + Actirob B + S3-1 + C9, Sapogenat + Hasten + S3-1 + C9, Sapogenat + Mero + S3-1 + C9, Sapogenat + Rako-Binol + S3-1 + C9, Sapogenat + Phytorob B + S3-1 + C9, Sapogenat + Edenor + S3-1 + C9, Sapogenat + Agnique + S3-1 + C9; Sapogenat + Actirob B + S3-1 + C10, Sapogenat + Hasten + S3-1 + C10, Sapogenat + Mero + S3-1 + C10, Sapogenat + Rako-Binol + S3-1 + C10, Sapogenat + Phytorob B + S3-1 + C10, Sapogenat + Edenor + S3-1 + C10, Sapogenat + Agnique + S3-1 + C10; Sapogenat + Actirob B + S3-1 + C11, Sapogenat + Hasten + S3-1 + C11, Sapogenat + Mero + S3-1 + C11, Sapogenat + Rako-Binol + S3-1 + C11, Sapogenat + Phytorob B + S3-1 + C11, Sapogenat + Edenor + S3-1 + C11, Sapogenat + Agnique + S3-1 + C11; Sapogenat + Actirob B + S3-1 + C12, Sapogenat + Hasten + S3-1 + C12, Sapogenat + Mero + S3-1 + C12, Sapogenat + Rako-Binol + S3-1 + C12, Sapogenat + Phytorob B + S3-1 + C12, Sapogenat + Edenor + S3-1 + C12, Sapogenat + Agnique + S3-1 + C12.

This results in a large number of possibilities of combining a plurality of agrochemical active substances with each other and employing them jointly for controlling harmful plants in plant crops without deviating from the spirit of the invention.

Thus, in a preferred embodiment, for example various herbicidal active substances of the formula (III) and/or their salts can be combined with each other, for example mesosulfuron-methyl + iodosulfuron-methyl,

mesosulfuron-methyl + iodosulfuron-methyl-sodium,

5 mesosulfuron-methyl + foramsulfuron,

mesosulfuron-methyl + foramsulfuron-sodium,

mesosulfuron-methyl-sodium + iodosulfuron-methyl,

mesosulfuron-methyl-sodium + iodosulfuron-methyl-sodium,

mesosulfuron-methyl-sodium + foramsulfuron,

10 mesosulfuron-methyl-sodium + foramsulfuron-sodium,

foramsulfuron + iodosulfuron-methyl,

foramsulfuron + iodosulfuron-methyl-sodium,

foramsulfuron-sodium + iodosulfuron-methyl,

foramsulfuron-sodium + iodosulfuron-methyl-sodium.

15

The herbicidal active substances c) and their mixtures, for example the abovementioned active substance mixtures of active substances of the formula (III) and/or their salts, can be combined with one or more safeners, in particular with the safeners mefenpyr-diethyl (S1-1), cloquintocet-mexyl (S2-1) and isoxadifen-ethyl

20 (S3-1).

The adjuvants according to the invention can not only increase the biological activity of agrochemical active substances, but also, in combination with agrochemical active substances and water, give a spray mixture with high physical stability.

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The adjuvants according to the invention show advantageous physical behavior on application. During the application, adjuvant and agrochemical active substance remain distributed uniformly in the spray tank, thus making possible uniform application to the crop or the area under cultivation. Mixtures which have formed in the spray tank, such as aqueous solutions, suspensions, emulsions or suspoemulsions, are stable, so that separation symptoms, such as irreversible creaming, sedimentation or agglomeration do not occur. Moreover, the adjuvants

according to the invention are economical and harmless from the ecological and toxicological point of view.

- The agrochemical compositions according to the invention show outstanding  
5 biological activity. These effects permit, inter alia, the application rate to be reduced, a broader spectrum of harmful organisms to be controlled, gaps in efficacy to be closed, more rapid and safer action, a prolonged long-term effect, complete control of the harmful organisms with only one or few applications, and a widened application window.

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The use examples which follow illustrate the invention and are in no way limiting.

#### Examples

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##### A. Preparation of the adjuvants

###### Example 1

20 950 g of rapeseed oil methyl ester were treated with stirring with 50 g of Sapogenat® T 080. 1000 g of the corresponding adjuvant according to the invention were obtained (Table 1, Ex. 1). Examples 2 - 15 were carried out analogously to Example 1.

25 Table 1 shows adjuvants according to the invention which had been prepared by mixing the components. In Examples 12 and 13, an emulsifier (Atplus® 309F, sorbitan-based surfactant mixture) was additionally admixed.

**Table 1:** Adjuvants according to the invention

<b>Ex.</b>	<b>Rapeseed oil methyl ester in % by weight</b>	<b>Surfactant Ia Sapogenat® T / % by weight</b>	<b>Surfactant Ib Sapogenat® T / % by weight</b>	<b>Others in % by weight</b>
1	95 %	080 / 5 %	-	
2	90 %	080 / 10 %	-	
3	90 %	080 / 5.85 %	040 / 4.15 %	
4	95 %	110 / 3.47 %	040 / 1.85 %	
5	95 %	110 / 4 %	040 / 1 %	
6	90 %	110 / 8 %	040 / 2 %	
7	84 %	110 / 10.4 %	040 / 5.5 %	
8	95 %	080 / 2.7 %	060 / 2.3 %	
9	90 %	110 / 7 %	020 / 3 %	
10	95 %	110 / 3 %	040 / 0.5 %	Atplus® 309F / 1.5 %
11	90 %	110 / 6 %	040 / 1 %	Atplus® 309F / 3 %
12	89 %	110 / 6.9 %	040 / 3.7 %	
13	90 %	080 / 5.4 %	060 / 4.6 %	

The adjuvants thus obtained are very economical and potent adjuvants.

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#### B. Application examples

The adjuvants according to the invention were tested for their usefulness in an application experiment. To this end, a spray mixture consisting of water, agrochemical active substance and the adjuvants according to the invention listed in Table 1 was prepared in a spraying apparatus. The spray mixture was then sprayed under the following conditions: stationary field sprayer (Hardy, 400 liter tank); pump capacity: 116 liters/min.: injector mixer with variable mixing intensity (15-50 liters/min); water hardness: 18 (German degrees of hardness); water temperature: 10°C; dosage: 0.15 kg MaisTer® granules (weight ratio foramsulfuron : iodosulfuron-methyl-sodium : isoxadifen-ethyl = 30 : 1 : 30); 2 liters of adjuvant; 75-100 liters of water; nozzles: 80 015 XR; stirring intensity: 30 liters/min; stirring time:

- 20 minutes after the sprayer has been charged with the spray mixture. After application of the spray mixture, the precipitates on the filters of the spraying apparatus, such as suction filters (50 mesh), pressure filters (80 mesh) or nozzle filters (100 mesh) were determined by visual scoring for assessing the usefulness of
- 5 the adjuvants according to the invention from the application aspect. The pore size of the filters is indicated in mesh.

Table 2 shows the test results. The precipitates on the filters are indicated in % of the filter area. The results confirm the outstanding usefulness of the adjuvants

10 according to the invention from the application aspect.

**Table 2:** Application experiments

Adjuvant	Sediments on suction filter [in % of filter area]	Sediments on pressure filter [in % of filter area]	Sediments on nozzle filter [in % of filter area]
Ex. 3, Table 1	1	3	3
Ex. 5, Table 1	1	0	3
Ex. 6, Table 1	1	0	2
Ex. 11, Table 1	0	0	0
Ex. 8, Table 1	1	1	5
Ex. 12, Table 1	1	0	5
Ex. 13, Table 1	0	0	1